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BLENDING STRATEGIES AND PROCESS MODIFICATION FOR THE FUTURE GASOLINE PRODUCTION

Master´s Programme in Advanced Energy Solutions
Major in Industrial Energy Processes and Sustainability

Master's thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 31st October 2019.

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Työn nimi Sekoitusstrategiat ja prosessin modifiointi bensiinin valmistukselle tulevaisuudessa

Maisteriohjelma Advanced Energy Solutions **Koodi** CHEM3044

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Päivämäärä 31.10.2019 **Sivumäärä** 71 **Kieli** Englanti

Tiivistelmä

Rekisteröityjen bensiiniautojen määrä kasvoi 6,5 prosenttiyksikköä Euroopassa vuonna 2018, mikä ennustaa bensiinintuotannon jatkuvan vielä useita vuosikymmeniä, vaikka sen haittapuolia ovatkin CO_2 päästöt, jotka kiihdyttävät ilmaston lämpenemistä. Tämän vuoksi tutkimuksen pitääkin keskittyä bensiinin uusiutuvien raaka-aineiden tutkimiseen, joiden ominaisuudet voivat kuitenkin erota fossiilisista. Tässä diplomityössä on kerätty laaja ominaisuustietokanta nykyisille bensiinin komponenteille, jota voidaan hyödyntää bensiinin sekoittamisessa tulevaisuudessa myös uusiutuvista raaka-aineista tuotetuille komponenteille optimoidessa sen korkeaa laatua.

Ominaisuustietokantaan kuuluvat bensiinin komponentit ja niiden ominaisuudet auttavat määrittämään jokaisen komponentin hiilivety rakenteen, fysikaaliset ominaisuudet sekä oktaaniluvut. Oktaaniluku, erityisesti tutkimusoktaaniluku (RON) on diplomityön pääominaisuus, johon keskitytään, koska se kuvaa bensiinin käyttäytymistä moottorissa. Tietokanta raportoi jokaisen bensiinin valmistuskomponentin RON:n, joissa huomataan eroavaisuuksia.

Diplomityön tulokset osoittavat, että bensiini koostuu yli 100 erilaisesta hiilivety yhdisteestä, kuten aromaateista ja parafiineista, sekä mahdollisesti myös alkoholeista ja eettereistä. Näillä yhdisteillä on huomattu olevan vaikutus RON:n, mikä johtuu niiden reaktiivisuuseroista. Suurempi reaktiivisuus laskee RON:a ja voi kasvattaa nakutuksen todennäköisyyttä moottorissa, joka voi aiheuttaa sen osien vaurioitumisen. Tulokset osoittavat, että parhaimmat yhdisteet nakutuksen estoon ovat aromaattiset sekä hapelliset yhdisteet. Diplomityön tulosten pohjalta huomataan, että kaksoissidoksen ja sivuryhmän paikoilla hiilivetyketjussa, ketjun pituudella ja OH-ryhmillä on vaikutus yhdisteen reaktiivisuuteen. Työssä huomataan erityisesti aromaattisten yhdisteiden metyyliryhmien paikalla olevan merkittävä vaikutus niiden RON:n. Aromaattiset yhdisteet, joiden metyyliryhmät ovat vierekkäisissä hiilissä, omaavat selvästi alhaisemman RON:n kuin ne, joilla metyyliryhmät ovat kauempana toisistaan. Nämä yhdisteiden rakenteelliset eroavaisuudet on tärkeää ottaa huomioon bensiinin valmistuksessa, koska ne voivat vaikuttaa lopputuotteen ominaisuuksiin.

Diplomityössä tutkitaan eri yhdisteryhmien oktaanien sekoittumista toistensa kanssa ja huomataan, että etanoli sekoittuu epälineaarisesti, mutta synergistisesti parafiinien ja olefiinien kanssa, mutta antagonistisesti aromaattien kanssa. Kuitenkin metyyliryhmien lisääntyessä aromaattisissa yhdisteissä, muuttuu sekoittuminen lineaarisemmaksi ja jopa synergistiseksi. Lisäksi diplomityössä esitetään uusiutuvia raaka-aineita, kuten terpeenejä ja furaaneja, joita olemassa olevat bensiinin jalostusyksiköt voisivat muokata tuottaakseen FQD:n mukaista ja samalla uusiutuvaa bensiiniä.

Avainsanat bensiini, bensiinin sekoittaminen, synergia, antagonismi, jalostus yksikkö, reaktiivisuus

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Title of thesis Blending strategies and process modification for the future gasoline production

Master programme Advanced Energy Solutions	**Code** CHEM3044
Thesis supervisor Annukka Santasalo-Aarnio	
Thesis advisor(s) Anna Karvo	
Date 31.10.2019 **Number of pages** 71	**Language** English

Abstract

The amount of the registered gasoline cars increased 6.5 percentage unit in Europe in 2018 that will forecast the gasoline production to continue still several decades, even though its drawbacks are the harmful CO_2 emissions that accelerate the global warming. Therefore, the research needs to concentrate on the development of the renewable feedstocks for gasoline. However, their problem could be the different properties compared to fossil gasoline. This master has collected the wide property database for the existing gasoline blending components that the gasoline blending can utilize to optimize the high-quality of gasoline also from the renewable feedstocks in the future.

With the help of the gasoline blending components and their properties in the database are identified the hydrocarbon structure, physical properties and octane numbers of each gasoline component. The octane number, especially research octane number (RON) is the main property that this master thesis concentrates because it defines the behaviour of gasoline in the engine. The database reports RONs for each gasoline blending components that differ from each other.

The results of the thesis show that the gasoline consist of over 100 different hydrocarbon compounds such as aromatics and paraffins and possible also of alcohols and ethers. These compounds have the highest impact on the RON that depends on their reactivity differences. Higher reactivity decreases the RON and increases the probability of knocking that could destroy the engine parts. The results show that the most viable organic compounds to avoid knocking are aromatics and ethanol.

There is noticed in the results of the thesis that positions of double bond and the side groups in the carbon backbone, the length of it and the OH-groups influence on the reactivity of compound. Especially, the positions of methyl groups in aromatics influence significantly on their RON. The methyl groups in the adjacent carbons decrease the RON of aromatics compared to those that have methyl groups further each other. These structural differences of the compounds are important to concern in the gasoline production, because they could affect to the properties of final product.

In the master thesis is researched the octane blending of different compound groups and noticed that ethanol blends non-linearly, but synergistic with paraffins and olefins, while the blending with aromatics is antagonistic. There is noticed the increase of methyl groups in aromatics to shift the blending more linear and even synergistic with ethanol. Moreover, thesis provides the outlook for the renewable feedstocks like terpenes and furans that the existing gasoline upgrading units could modify to fill the requirements of FQD and simultaneously produce renewable gasoline.

Keywords gasoline, blending of gasoline, synergistic, antagonistic, upgrading unit, reactivity

Preface

This master thesis is a part of the Digifuels project between Aalto University and Neste Oyj. The purpose of the thesis was to build the property database for gasoline blending components that provides input data for the development of the Fuel Blend Property Calculator in the future. It has been accomplished at the research group of the Energy Conversion and Neste Technology Center.
I would like to thank my supervisor, professor Annukka Santasalo-Aarnio from Aalto University to provide me this very interesting topic and to be part of this extremely versatile project. I would like to thank her and my advisor Anna Karvo from Neste for their valuable feedbacks and ideas to improve my thesis. Moreover, I learned a lot about gasoline and its production that I want to thank my advisor. I would like to thank also Juha Keskiväli and Ulla Kiiski for their feedback for my thesis during my summer in Neste and all colleagues who I worked with at the Neste Technology Center and Aalto University.
Finally, I sincerely thank my parents, Elina and Timo, for all the support along my educational journey and, my grandmother, for her encouragement during my university studies. Especially, I want to thank my father for the patience to solve the mathematical calculations with me and my mother to listen our constructive debates. In the end, I am especially grateful to my boyfriend and my awesome friends for these memorable years in the Aalto University.

Otaniemi, 31.10.2019

Lotta Knuutila

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Abbreviations

AKI	Anti Knock Index
BDE	Bond dissociation energy
CMF	5-choloromethylfurfural
CST	Crude sulphate turpentine
CO	Carbon monoxide
DMF	2,5-dimethylfuran
DVPE	Dry Vapour Pressure Equivalent
ETBE	Ethyl tert-butyl ether
FAME	Fatty acid methyl ester
FBPC	Fuel Blend Property Calculator
FCC	Fluid catalytic cracking
FQD	Fuel Quality Directive
GC	Gas Chromatography
GHG	Greenhouse gas
HCl	Hydrogen chloric
HDO	Hydrodeoxygenation
HHV	Higher heating value
HMF	5-hydroxymethylfurfural
HOV	Heat of vaporization
HVO	Hydrotreating of vegetable oils
LHV	Lower heating value
LIMS	Laboratory management system
MIBK	Methyl-isobutyl ketone
MTBE	Methyl tert-butyl ether
MON	Motor octane number
NaCl	Sodium Chloride
NEXBTL	Next Generation Biomass To Liquid
NMS	Neste management system
NOx	Nitrogen oxides
PAHs	Polycyclic Aromatic Hydrocarbons
PONA	P(paraffinic), O(olefinic), N(naphthenic), A(aromatic)
PVC	Polyvinyl chloride
RON	Research octane number
SI	Spark-ignition
TAEE	Tert-amyl ethyl ether
TAME	Tert-amyl methyl ether
V/L	Vapor-to-liquid
VLI	Vapour Lock Index

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1 Introduction

The global warming is the key topic today, and one of the industries that especially need to prevent it is the oil refining. The oil consumption is today 94 million barrels per day and its production has been predicted to increase in next decades (OECD, 2019). The reasons for this increase are the changes in the lifetime and the growth of the population (Masum et al., 2013). However, this increasing consumption will add the greenhouse gas (GHG) emissions that demands research of the new feedstocks to produce fuels. For instance, biomass could be a promising option, because it is a renewable and it has a wide availability compared to solar or wind, which the weather fluctuations limits strongly (Harjanne and Korhonen, 2019). Biomass can be labelled as 1st generation such as corn and wheat, and 2nd generation sources such as forest residues and wastes (Dutta et al., 2014). The Finnish oil refining company, Neste, is the leader and the biggest renewable diesel producer utilizing 2nd generation feedstocks such as wastes and residues (Neste, 2016). Moreover, the other solutions for the future fuel production could be found from the 3rd and 4th generation feedstocks such as algae and CO2 (Dutta et al., 2014).

European commission has also own targets to decrease transport-related GHG emissions by 20% from the levels of 2008 by 2030 and by 60% from the levels of 1990 by 2050. The procedures to decrease those emissions are prohibiting the conventionally-fuelled cars in the cities, decreasing 40% of CO2 emissions from maritime bunker fuels and increase sustainable low-carbon fuels in the aviation (European Commission, 2019). Today, in Finland, the share of biofuels in the transportation is only 12% of fuels, but the ambitious target is to increase the share by 30% by 2030 (Koistinen, 2018).

Gasoline is the refinery product that consists of hundreds of different hydrocarbons such as paraffins and aromatics that form gasoline blending components. The refineries blend these components to maximize the high quality of gasoline and to follow the Fuel Quality Directive (FQD) and standards. (Totten et al., 2003.) The most important properties of commercial gasoline are for instance, vapour pressure, heating value, aromatic and sulphur contents. Moreover, the octane number is the main quality character of gasoline that describes its knocking tendency. (El-Fattah et al., 2008.) Octane number has two different indicators, research octane number (RON) and motor octane number (MON) that differ from each other by the test conditions.

In the future, the target of developing of the modern spark-ignition (SI) engines is to have high-efficient engines that can utilize gasoline during combustion completely to reduce emissions. Therefore, the properties of gasoline need to be favourable that its ignition behaviour in the engines is proper and the harmful autoignition reactions could be avoided. The autoignition of gasoline causes the knocking that most of the modern

SI engines detect by their knock-sensors. Those sensors inform the engine management system that usually in turn retards the ignition timing. However, the retardment of ignition timing reduces the power of the engine. Therefore, gasoline needs to have high antiknock facility to avoid the knocking and the power loss. The high difference between RON and MON improves antiknock facility and therefore, gasoline with high RON and low MON is favoured. (Kalghatgi, 2015; Kalghatgi, 2001).

To produce gasoline with high knocking resistance demands blending of suitable gasoline components from the different refinery upgrading units. However, the blending is not easy, because blending components have different RONs due to their chemical structure. The purpose of this master thesis is to collect wide property database of gasoline blending components to describe their hydrocarbon structure, physical and chemical properties and octane numbers. Master thesis applies the data of the hydrocarbon structure to explain the variations among RONs between different hydrocarbon groups that explain the blending behaviour of different gasoline blending components. The analysis provides input data for the building of the Fuel Blend Property Calculator (FBPC) for gasoline in the future that will enhance the optimization of RON in every day gasoline production in the refineries.

Moreover, as the target is to reduce oil consumption in the future, the renewable feedstocks for gasoline need to be researched. These feedstocks contain different chemical structures and functionalities than crude oil and therefore, defining these functionalities and modifying the feed in the refinery units to produce more sustainable gasoline should be the target in the future. This master thesis will provide an outlook of the feed modifications and their possible reactions in the existing gasoline upgrading units to produce renewable gasoline.

1.1 Thesis structure

This Master thesis is divided to literature part and the research part. The literature part introduces first gasoline, its blending components and their production units in the refinery. Then, it presents gasoline regulation in the EU, the chemical composition of gasoline blending components and the properties of gasoline.

Chapter 3 researches the chemistry of hydrocarbons in detailed to provide explanations for the variations between RONs among different hydrocarbon groups. Moreover, it explains the differences between linear and non-linear blending. Chapter 4 divides the future renewable feedstocks to four generations and introduces possible feedstocks for the renewable gasoline production.

The research part collects the data from Neste LIMS software to create the database for the properties of gasoline blending components that predicts the final gasoline properties. Chapter 5 explains how the database is collected and which properties are researched. Chapter 6 reports the results of hydrocarbon compounds of gasoline and their RONs, presents the properties of database for every blending component and

shows their variations. It indicates the importance of the property of gasoline components on final gasoline. Chapter 6 shows also possible renewable feedstocks, their reactions mechanisms and products in the existing gasoline upgrading units to produce renewable gasoline. In the end, it presents the results of possible blending proposals according to the blending behaviour of hydrocarbons and other organic compounds.
The master thesis answers to the next questions:

1. What is the chemical structure of gasoline blending components and how it explains their RON?
2. How the properties vary among gasoline blending components and what is the significance of properties for gasoline?
3. Which compounds blend non-linearly?
4. Which renewable feedstocks are possible to upgrade in the existing gasoline units?

2 Gasoline

Gasoline has hundreds different hydrocarbon molecules that consist of 4 to 14 carbon atoms per molecule (Totten et al., 2003). It is standard SI- engine fuel that automobiles and light trucks apply (Kroyan, 2018; Schobert, 2013). The raw materials for it are different crude oils or their mixtures that are upgraded in the many steps to obtain blending components. These components are then blended to produce high quality gasoline product according to the national laws, the FQD and country- specific standards (Totten et al., 2003; Olsen, 2014).

2.1 Crude oil

Crude oil is the raw material for fossil-based gasoline and consists of tens of thousands of hydrocarbons that can be categorized into aromatic, paraffinic and naphthenic hydrocarbons (Schobert, 2013). In addition, metals, heteroatoms such as sulphur, and oxygen are included in to crude oil (Totten et al., 2003). High-quality fuel products are refined from it through the many process pathways that include washing stage, fractionators, reactors and distillation columns, for instance (Olsen, 2014).
The quality of crude oil varies a lot according to its properties such as relative density, levels of metals and sulphur. Its supply is depending on the current infrastructure and economy. However, the lack of crude oil with specific feed properties is possible to substitute by blending multiple crude oils together to achieve a feedstock that completes the requirements of refinery. (Olsen, 2014; Totten et al., 2003.)

2.2 The refinery processes

From crude oil to gasoline is a multi-phase process pathway that has different units where the fractions of crude oil are separated by distillation. These fractions react with other fractions or for instance, with hydrogen, in separate upgrading units such as hydrotreating, reforming and alkylation unit that have one or more reactors to produce chemically different gasoline components. Moreover, some refineries have an ether-units to produce Methyl tert-butyl ether (MTBE) or Ethyl tert-butyl ether (ETBE) and tert-amyl-methyl ether (TAME) or tert-amyl-ethyl ether (TAEE).
There are presented the main conversion and upgrading units of crude oil refining in the next sections. Examples of units are hydrotreating that removes impurities such as sulphur and hydrogenates double bonds to produce paraffins as product or for further upgrading units. Also, isomerization is the upgrading unit that isomerases n-paraffins into more branched isoparaffins and decyclizates naphthenes. Moreover, reforming, fluidized catalytic cracking (FCC) and alkylation increase octane number of gasoline adding aromatic, olefin and isoparaffin structures into it.

2.2.1 Crude oil preparation and separation

Crude oil is first stored in the large tanks at the refinery area and after that in the first stage, mixing water in the desalter vessel removes its salts and sediments. The importance of removing them is the protection of equipment from the corrosion, and fouling and, moreover, they are catalysts poisons. (Olsen, 2014.) Especially, sodium chloride (NaCl), is the most harmful salt in crude oil, because it can react with hydrogen forming hydrochloric acid that causes corrosion on the equipment. (Schobert, 2013.)
Before the crude oil is fed to the next stage, atmospheric crude fractionator, the furnaces preheat it up to 340-410 °C (Totten et al., 2003). It is important to keep the temperature on the range otherwise thermal cracking could occur that increases the production of carbon deposits on the pipes and equipment that might lead in the worst case to shutdown of the process (Olsen, 2014).
In some refineries, before atmospheric fractionator, is a preflash column that removes lower boiling point components (Totten et al., 2003). The atmospheric crude fractionator separates the desalted crude oil into fractions according to boiling point ranges. The fractions are typically light naphtha, heavy naphtha, kerosene, diesel oil, lubricating oil, fuel oil and residue. Figure 1 presents the fractions, their temperature ranges and shows the typical boiling point fraction for gasoline to be between 32 and 165 °C.

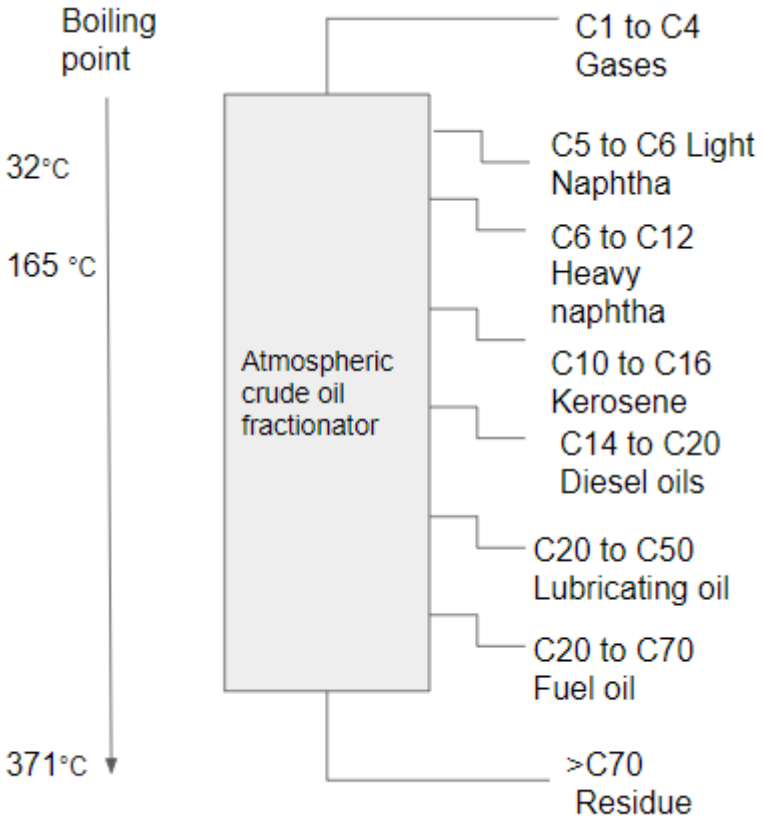

Figure 1. The boiling points of different fractions from the atmospheric crude distillation.

The lighter fractions in Figure 1 belongs to gasoline production, such as light naphtha and heavy naphtha, while diesel oils and kerosene have longer hydrocarbon chains and therefore, higher boiling points. The heaviest parts of crude oil are collected from the column plate and the vacuum distillation separates them.

The boiling points of fractions do not change, but the flowrates will change based on the utilized crude oil feedstock (Olsen, 2014). After atmospheric distillation side strippers purify the impurities from the fractions and, also separate strippers remove volatile parts of them. These volatile compounds are then returned to atmospheric crude distillation and the purified fractions are feedstocks into the gasoline upgrading units. (Schobert, 2013.)

The vacuum fractionator separates heavy, higher boiling point components under the vacuum that prevents thermal cracking. Steam inside the fractionator prevents fouling of the equipment and improves vaporization of heavy components at the bottom of the fractionator. The temperature range in the vacuum fractionator is between 540-565 °C or even 575 °C that it is larger compared to atmospheric crude fractionator, because the occupied volume of vaporized crude oil is larger. Its fractions based on the boiling points are light vacuum gas oil, medium vacuum gas oil and heavy vacuum gas oil that is further processed in the FCC unit. (Olsen, 2014; Totten et al., 2003.)

2.2.2 Processes and blending components for high quality gasoline

This section presents gasoline components and their production units that Figure 2 shows in its block diagram. After the atmospheric crude distillation, the different upgrading units produce gasoline, diesel and kerosene from the separated fractions.

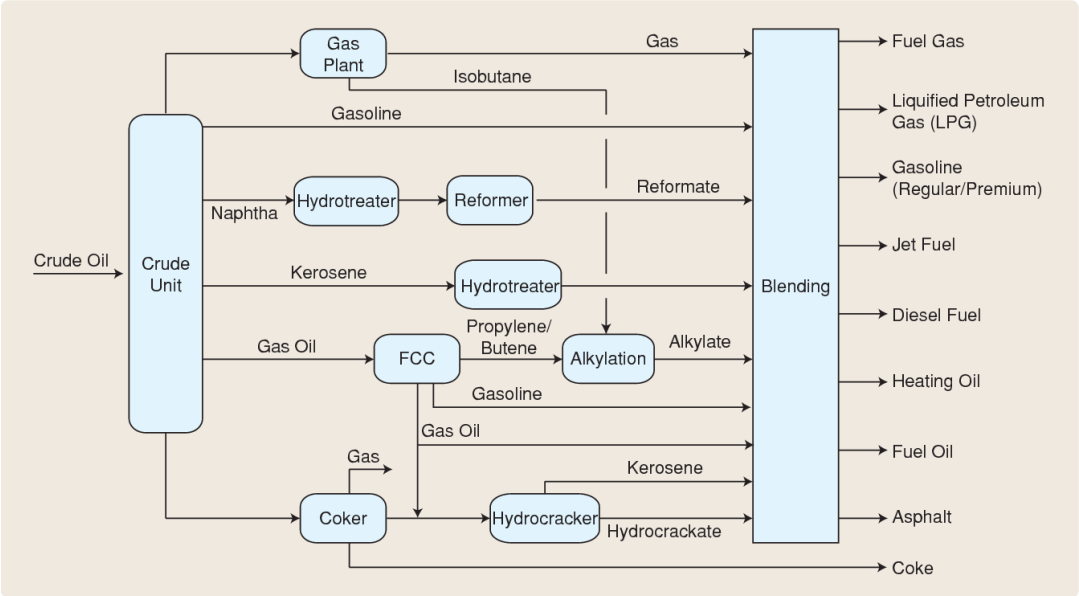

Figure 2. The refining of crude oil into refinery products (Young, 2006).

From Figure 2 can be seen how complex the oil refining process is and how many possible products it produces. The most important units for gasoline production are hydrotreaters, reformer, FCC and alkylation. Beside these, the isomerization and ethers units exist in some refineries.

Sulphur removal

The regulation limits strictly sulphur content in fuels and therefore, the refineries need to have the suitable unit to remove it. The refineries could have more than one sulphur removal unit, however, the basic principle is the same: unit cleans heavy and light naphtha from impurities.

The hydro-desulphurization removes sulphur compounds and, in addition, hydrogen sulphide and mercaptans, bad smelling gas. The reactions hydrogenate sulphur compounds away and, also beside hydrogenates double bonds of the feedstock. (Owen and Coley, 1995.) Therefore, the units stand before reforming and FCC unit to reduce the amount of olefins in their feed.

The absorption concentrates removed hydrogen sulphide into amine solution. Amine regenerator releases hydrogen sulphur from it and leads it to a sulphur recovery unit that collects elemental sulphur. (Olsen, 2014.)

The sulphur removal unit has also other part, the fraction distillation unit, that separates C3-C4 fractions, heavier hydrocarbons C7-C11, hexane and pentane from the feed. Heavier fractions are fed into reforming unit and, they are also possible to use as gasoline blending components. (Owen and Coley, 1995.) N-butane releases from sulphur removal unit after gasoline stream is hydrotreated from sulphur and it is valuable gasoline blending component, especially in the winter times. It increases the vapour pressure that ensures the ignition of gasoline in the cold weather. (Olsen, 2014.)

FCC

The function of FCC is to break long-chain, C20-C70, heavy gas oils and residues into lighter and shorter, naphtha-boiling-range hydrocarbons (Totten et al., 2003). Moreover, the low sulfuric gas oil products can be used as a feedstock to the FCC unit to increase its conversion. The FCC unit produces gasoline component called Cat gas that has high octane number. (Olsen, 2014.) The unit is the one most utilized in the oil refinery to convert heavy oils into lighter and more valuable products (Schobert, 2013), but it is also the most challenging to operate, because it has specific process dynamics. Refineries have different versions of FCC depending on the builder and licensor, however, the operation principles are similar of these units. The unit consists of a reactor, a catalyst regenerator and a main fractionator column at the downstream and, also a series of distillation columns. (Olsen, 2014.) The capability to vary yield and composition of the blending components explains the popularity of FCC unit (Totten et al., 2003).
The main factor for the high quality of blending component is the reaction mechanism that utilizes the positive-charged carbocations, carbonium or carbenium ions, not radicals (Schobert, 2013). The carbocations are formed when regenerated catalyst is in contact with heavy gas oil feed. Equation 1 presents the formation of carbocations when hydrogen ion reacts with paraffin molecule. (Sadeghbeigi, 2012.)

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 + (H+) \rightarrow R\text{-}(C+)H\text{-}CH_2\text{-}CH_3 + H_2 \quad (1)$$

The charge of carbonium ions is unstable and therefore, they are not common carbocations in the FCC unit. While carbenium ions are more probable carbocations that are formed by removing hydrogen and two electrons form paraffins. Moreover, their formation from olefins is possible by adding a positive charge to them. (Sadeghbeigi, 2012.) Equations 2 and 3 show the reaction mechanism of these two reactions.

$$R\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightarrow R\text{-}(C+)H\text{-}CH_2\text{-}CH_3 \quad (2)$$

$$R\text{-}CH{=}CH\text{-}CH_2\text{-}CH_3 + (H+) \rightarrow R\text{-}(C+)H\text{-}CH_2\text{-}CH_3 \quad (3)$$

The three most common reactions in the FCC unit are cracking the C-C -bond, isomerization and hydrogen transfer. Moreover, cyclization, coking and dehydrogenation are possible reaction in this unit. The C-C -bond cracking, also called beta scissions, breaks the low energy bond between carbon atoms to form two shorter hydrocarbon chains. The main product from beta scission is olefin that is desired product for further units and, it also increases octane number of Cat gas component. (Sadeghbeigi, 2012.) The beta scission reactions favour high temperatures and therefore, catalyst and feed react at 525-550 °C. Other reaction type in the FCC unit is isomerization that breaks the bonds also via beta-scission and forms tertiary ions that are the most stable carbocations that boost the branching during cracking and increase octane number. (Sadeghbeigi, 2012.)

Third reaction in the FCC unit is the hydrogen transfer that transfers hydrogen from olefin to olefin to form paraffins and cyclo-olefins. Cyclo-olefin reacts further and rearranges to ended up aromatic that has not further reactions due its high stability. The hydrogen transfer reaction can also occur between olefin and naphthene where hydrogen transfers from naphthene to olefin to form paraffin and aromatic. (Sadeghbeigi, 2012.) Table 1 concludes the possible hydrocarbon structures in the feed and shows their reaction pathways.

Table 1. The reaction pathways from different feed compositions to FCC products (Sadeghbeigi, 2012).

Feed	Reactions
n-paraffins	Cracking of long n-paraffins into C6-C7 paraffins
olefins	H-transfer and quick double-bond shifts
naphthenes	Cracking
alkyl-aromatics	Cracking of the alkyl group next to the aromatic ring

Table 1 shows that the most typical feedstocks are n-paraffins, olefins, naphthenes and alkyl-aromatics and the cracking is the dominant reaction for their modification. It applied catalyst to execute these reactions which average catalyst flowrate is around one ton per thousand barrels of oil feed (Olsen, 2014). The most utilized catalysts are zeolites that are large family of aluminosilicates, have high reactivity and therefore, manages to process the low-quality feed. (Totten et al., 2003). The zeolite catalysts consist of one fourth of zeolite crystals that are embedded in a matrix of silicon and aluminium oxides. The silica-aluminium matrix decreases the price of zeolite and the

demand of well-designed heat transfer to maintain the safe operation. (Schobert, 2013.) However, the polymerization of olefins and aromatics in the reactor forms coke that settles on the fluidized catalyst particles and decreases the catalyst activity. Therefore, the regenerator continuously burns coke from top of the contaminated catalysts to flue gases. (Totten et al., 2003.)
In the downstream of the reactor is the main fractionator column that separates, and recoveries cracked hydrocarbon vapours from the reactor. The products from column are light gases, liquefied gas (propane and butane), gas oil, light absorber gas oil, base oil and gasoline blending component, Cat gas. The series of distillation columns treat liquids from overhead receiver of the main fractionator column to clean gasoline fraction from light gases and the rest of gases are separated into olefins, ethane and fuel gas. (Olsen, 2014.)

Catalytic reformer

There are paraffins, aromatics and naphthenes in the feed of the reforming unit from which aromatics and naphthenes facilitate the reforming mostly. Otherwise olefins are not desirable in the feed, because they polymerizate and produce coke that deactivates catalyst. The product from the catalytic reforming is called reformate that consists mainly of high-octane aromatics that varies depending on the applied amount of hydrogen. (Schobert, 2013.)
The partial pressure of hydrogen is a significant factor for properties of reformate, because its low partial pressure favours the production of aromatics, but also increases the coke formation. While high partial pressure of hydrogen boosts hydrocracking and decreases the production of high-octane aromatics, that the operation of unit tries to avoid. (Schobert, 2013.)
Nowadays, the most suitable reactor configuration is the continuous that removes formed coke during hydrogenation continuously and thus, the operation pressure in the reactor stays low. This ensure the maximum hydrogenation of naphthenes to aromatics that will produce high-quality reformate. (Totten et al., 2003.)

Isomerization unit

In the refinery the isomerization unit isomerizes n-paraffins into isoparaffins at the presence of excess hydrogen and catalyst. Moreover, the saturation of benzene produces naphthenes. The purpose of isomerization is to improve properties of gasoline and increase the octane number by adding more branching. (Kroyan, 2018; Sadeghbeigi, 2012; Olsen, 2014; Totten et al., 2003.)
The feed to the unit comes from the atmospheric distillation of crude oil after its pretreatment. It typically consists mainly of C5-C9 paraffins, lighter alkyl cycloalkanes and alkyl aromatics. (Schobert, 2013.) The feed is heated in the reactor with recycled

hydrogen to 180-260 °C and after that it flows to the fixed bed reactor where it reacts in the presence of catalyst. After that the tall distillation column separates n-paraffins from isoparaffins. The separation is difficult, because paraffins have almost the same boiling points, n-paraffins slightly higher. (Olsen, 2014.)

Alkylation unit

In the alkylation unit isobutane reacts with olefins and produces C8 isoparaffins such as iso-octanes. The feedstocks are usually the side streams from the other upgrading units like FCC, MTBE and hydrotreating. The alkylation operates with acid catalyst, either sulphuric or hydrofluoric acid that requires low temperature 0-40 °C and high isobutane-to-olefin ratio. (Olsen, 2014.)

The alkylation is simple to implement: liquefied hydrocarbon feeds mix with strong acid and finally, the alkylate is separated from the catalyst. In the reality the alkylation involves a lot of observation, because it forms acid-hydrocarbon molecules that is an exothermic reaction. Moreover, the operation needs prevent polymerization of olefins, high catalyst consumption and consider the safety issues. (Totten et al., 2003.) However, the new alkylation technologies concentrate more on the safety using different types of catalysts such as ionic liquids and thus, eliminate the risks of acids. Ionic liquids offer more safer, environmentally friendly and efficient catalyst for the alkylation of isobutane and butene, because they reduce the strong acid consumption. There are still drawbacks like the high price, the sensitivity to moisture and the high viscosity in the use of these catalysts. (Wang et al., 2017.)

Finally, alkylates are collected from the column plate for gasoline blending, n-butane is collected as a side stream as well the iso-butane from top of the column (Olsen, 2014). Alkylate is a paraffinic blending component that has octane number approximately 95 (Schobert, 2013).

Hydrocracking

The hydrocracking was before the primary unit to maximize the production of gasoline, but nowadays the hydrocracker produces mainly low-sulphur diesel and jet fuel. It is not a necessary part of the refinery and its use also increase the maintenance cost and hydrogen consumption. However, the absence of hydrocracking units causes lack of hydrogen that refineries need to cover by other ways such as building the hydrogen generation plant or purchasing it outside. The hydrocracking unit includes a product fractionator that separates diesel, gasoline and light gases. The cracking reactions are endothermic while the whole process is exothermic, because the hydrogenation reactions occur simultaneously in the reactor. (Olsen, 2014.)

Ether units

Ethers are gasoline blending components that have oxygen in their structure and thus, their production involves alcohols in addition to crude oil. MTBE has been used as a blending component already in the 1980 and it is still one of the most used gasoline components. However, its use is highly discussed especially in USA, because it leaked from underground storage tanks into groundwater around twenty years ago. Because of this leakage, the state of California for instance, banned its use in 2003. (Totten et al., 2003; Rausser et al., 2005; Topgül, 2015.) The FQD limits the maximum ether addition into gasoline at 15 vol% for 98E5 and at 22 vol% for 95E10. (Totten et al., 2003; 2009/30/EC, 2009.)

Usually, MTBE is produced in the process unit that is in front of the alkylation unit that offers the C4 paraffinic and olefinic stream into it. (Owen and Coley, 1995; Totten et al., 2003.) Normally, the same unit produces ETBE by changing the methanol to ethanol. The advantages to use MTBE and ETBE as a blending component are their ability to decrease hydrocarbon and carbon monoxide (CO) emissions and decrease the number of toxic components, like benzene. Moreover, the RONs of MTBE and ETBE are 115 and 110 that refers their high antiknock resistance. However, the nitrogen oxides (NOx) emissions could increase, because their high oxygen concentration causes lean combustion. (Topgül, 2015; Owen and Coley, 1995.)

The mixture of C4-C7 olefins with methanol produces TAME and with ethanol TAEE (Owen and Coley, 1995). These ethers are viable gasoline blending components as well, because they have high RONs, 111 and 105 (Owen and Coley, 1995). Normally, the refineries have one unit to produce TAME and TAEE that changes only the methanol to ethanol during the TAEE production.

Coker

In the delayed coker, occurs the cracking of thermally heavy feedstocks from vacuum fractionator to produce solid coke, heavy gas oil, light gas oil and coker gasoline that is a possible gasoline blending component. First, the fired heaters heat the mix of bottom of vacuum distillation, then they are guided with steam t to the online coke drum that thermally cracks the liquid into coke and other vapour products. Normally, the refineries have two coker drums that operates in turns in 24 hours cycles. Without coker refinery can sell their vacuum residue to other refineries for asphalt production or produce it by themselves. (Olsen, 2014.)

2.3 Other gasoline blending components

This section presents blending components that the upgrading units in the previous section does not produce. These blending components are renewable gasoline component, ethanol, n-butanol and isobutanol.

Neste My Renewable Gasoline

Neste My Renewable Gasoline™ is gasoline blending component that is a by-product from production of MY Renewable Diesel™. The raw materials for its production are wastes and residues and it is sulphur- and aromatic free component that has higher energy density than ethanol. (Neste, 2019a)
There are mainly n-and isoparaffins in Neste My Renewable Gasoline™ component that causes its low density, approximately 670 kg/m^3. Moreover, its vapour pressure is 18.5 kPa and the boiling range 40-170 °C. (Neste, 2019b)

Ethanol

Because of high RON of ethanol, apply refineries it as gasoline blending component. Ethanol decreases the carbon footprint of the fossil gasoline, because the raw material for its production is for instance sugar cane. However, the large-scale production of ethanol for gasoline considers still many problems such as energy balance and 1st generation feedstocks. The feedstocks of ethanol such as sugar cane and corn, are the 1st generation feedstocks that compete with the food production. Moreover, the production of ethanol for gasoline is not in the energy balance, because its production requires more energy than it releases during combustion in the engine. (Schobert, 2013.)
The maximum ethanol addition to 98E5 gasoline is 5 vol% and 95E10 is 10 vol% according to the FQD. (2009/30/EC, 2009.) In the future, the larger additions of ethanol could be possible way to add renewable gasoline production. However, the increase of ethanol content above the 10 vol% in the blends, could the heating value of gasoline decrease that increases gasoline consumption in the consumer point of view. The lower heating value (LHV) of gasoline is 32 MJ/l, while ethanol has only 21 MJ/l (Neste, 2015). However, the driving style, weather and road conditions and traffic have the main influence on the gasoline consumption and the heating value of gasoline below 10 vol% concentration of ethanol is a minor effect. (Masum et al., 2015.)
The boiling point of ethanol is 78 °C, while conventional hydrocarbon gasoline boils typically between 30-210 °C. The similar volatility of ethanol provides its proper operation during warm-up and start-up in the SI engines. However, the flash point of ethanol is 12.8 °C, while gasoline has around -40 °C. The flash point of gasoline covers

the temperature range that ensures the ignition of gasoline even in the very cold conditions, but the flash point of ethanol is significantly higher that might cause problems for gasoline ignition in the winter. (Schobert, 2013.)

N-Butanol and isobutanol

N-butanol is possible liquid biofuel because of its energy density is 26.9 MJ/l that is higher than ethanol. The FQD approves its use as gasoline blending component and limits its use up to 15 vol% in gasoline blend. The vapour pressure of n-butanol is lower, and its corrosive effect to engine system is smaller compared to ethanol. The process pathways that utilize biomass wastes and engineered microalgae could produce renewable n-butanol. (Lü et al., 2011; Liu et al., 2019.)
N-butanol, as also other oxygenated compounds, reduces the particulate emissions and CO emissions, while NOx and hydrocarbon emissions might increase. With the careful selection of the air-fuel ratio, is it possible significantly reduce the emissions compared to fossil-based gasoline. However, the addition of n-butanol increases the formaldehyde and acetaldehyde emissions like other alcohols do as well. Moreover, the large-scale preparation of n-butanol is still expensive. (Liu et al., 2019; Qian et al., 2015.)
Isobutanol has almost the same energy density than n-butanol and both have higher than ethanol, because oxygen-to-carbon ratio is lower compared to it. The FQD also limits the use of isobutanol as a blending component in gasoline blend up to 15 vol% (2009/30/EC, 2009). It has RON 106 and in addition, it is insoluble in water, because its longer carbon chain. The addition of these butanols 12 to 15% into gasoline blend has been noticed vapour pressure to decrease approximately 7 kPa that will help to produce low vapour pressure gasoline in the summer. (Tao et al., 2014.) The cyanobacteria are possible raw materials for the isobutanol production in the future (Aro, 2016).

2.4 Gasoline regulation

EU, nations and sometimes city and municipal level regulate gasoline. The FQD is a specification of legislation that instructs gasoline, diesel and biofuels in road transport and gasoil in non-road-mobile machine. EU demands that the fuel quality meets the strict requirements to protect the environment and human health. Therefore, the member states of the EU need to follow FQD and implement its content in their legislation. (2009/30/EC, 2009.)
Unleaded gasoline is standardized by EN 228 standard that guides the implementation of FQD. The EN 228 standard has two instructions for the FQD depending on the oxygen contents in gasoline that are of 2.7 wt% or 3.7 wt%. (SFS-EN 228: 2012 +

A1:2017, 2017.) Table 2 lists the current requirements of highway gasoline based on the FQD and EN 228 standards.

Table 2. The requirements of highway gasoline in the EU based on the FQD and EN 228 standard (2009/30/EC, 2009; SFS-EN 228: 2012 + A1:2017, 2017).

Parameter	Directive 2009/30/EC Gasoline	EN 228 standard, 2017 for unleaded gasoline with a maximum oxygen content of 3.7 wt%	EN 228 standard, 2017 for unleaded gasoline with a maximum oxygen content of 2.7 wt%	Unit
RON	min. 95	min. 95	min. 95	
MON	min. 85	min. 85	min. 85	
DVPE (summer)	max. 60	max. 60	max. 60	kPa
	max. 70, if the ambient summer temperature is low	max. 70, if the ambient summer temperature is low	max. 70, if the ambient summer temperature is low	
DVPE (winter)	-	max. 80	max. 80	kPa
		max. 90, if the ambient winter Temperature is low	max. 90, if the ambient winter temperature is low	
Distillation				
Percentage evaporated at 100 °C	min. 46	min. 46	min. 46	vol%
	max. 72	max. 72	max. 71	
Percentage evaporated at 150 °C	min. 75	min. 75	min. 75	vol%
Final boiling point	210	210	210	°C
Density	-	min. 720; max. 775	min. 720; max. 775	kg/m^3
Sulphur content	max. 10	max. 10	max. 10	mg/kg
Lead content	max. 5.0	max. 5.0	max. 5.0	mg/l
Manganese content	-	2	2	mg/l
Oxidation stability	-	360	360	minutes
Copper strip corrosion (3h at 50 °C)	-	class 1	class 1	rating
Appearance	-	clear and bright	clear and bright	Visual inspection
Existent gum content (solvent washed)	-	max. 5.0	max. 5.0	mg/100 ml
Oxygen content	max. 3.7	max. 3.7	max. 2.7	wt%
Olefins	max. 18	max. 18	max. 18	vol%
Aromatics	max. 35	max. 35	max. 35	vol%
Benzene	max. 1.0	max. 1.0	max. 1.0	vol%
Ethanol	max. 10	max. 10	max. 5.0	vol%
Methanol	max. 3.0	max. 3.0	max. 3.0	vol%
Isopropyl alcohol	max. 12	max. 12	Volume blending restricted to 2.7 wt% maximum oxygen content	vol%
Ethers containing at least five carbon atoms	max. 22	max. 22		vol%
Tert-butyl alcohol	max. 15	max. 15		vol%
Isobutyl alcohol	max. 15	max. 15		vol%
Other oxygenates	max. 15	max. 15		vol%

What stands out clearly in Table 2 are many technical limits for gasoline that regulate its blending. Therefore, the blending must be designed to meet the technical and composition limits. Table 2 shows the limit for ethanol to be 5.0 vol% for 98E5 gasoline and 10 vol% for 95E10 gasoline that could rise in the future, if the ethanol concentration increases up to 20-25% in gasoline blends. This addition influences on other gasoline properties such as density, volatility, octane number and oxygen limit. Nowadays, the oxygen limit is 2.7 w% and 3.7 w%, but if the ethanol limit rises to 20 and 25%, the linearly calculated oxygen limits would be 7.4 wt% and 9.25 wt%. Gasoline would be heavier with the higher addition of ethanol than 10 vol% and therefore, the density limit could increase as well. Moreover, ethanol increases the vapour pressure rapidly with the low concentrations, but with the higher concentrations than 10 vol% of ethanol, vapour pressure starts decrease. (Davidson, 2013.)

2.5 Hydrocarbons

Chemical groups of crude oil consist of basic types of hydrocarbons: paraffins, olefins, naphthenes and aromatics. The differences between structures are the amount of bonds between carbons and the shape of molecules, ring or chain. Carbon atom has four electrons in its outer shell that it wants to complete to obtain octet structure. Therefore, carbon atom needs to form bonds with other carbons, atoms or molecules to have stable structure. These bonds can be single, double or triple bonds and normally, in the gasoline refining, carbon has single or double bonds with other carbon atoms and rest of the bonds between hydrogens or other elements such as oxygen, sulphur or nitrogen. (Totten et al., 2003.)
Hydrocarbon that has single bonds between carbons is called saturated, while hydrocarbon with double bonds is unsaturated. Paraffins and naphthenes are saturated hydrocarbons, while olefins and aromatics are unsaturated.

2.5.1 Paraffins

Paraffins are saturated, straight or branched chain hydrocarbons in the gasoline blend. Their content is usually between 30-60% of the blend and desired paraffins are branched paraffins, also called isoparaffins, because their higher-octane number. Isomerization of n-paraffins into isoparaffins is possible reaction pathway in the refinery to increase the octane number of blending components. (Olsen, 2014.) Moreover, cracking of long paraffins into shorter, gasoline boiling range hydrocarbons is the viable reaction pathway, but its drawback is the high production of coke that reduces the activity of catalyst. (Totten et al., 2003.)
Cyclic paraffins are called naphthenes that consists of at least 5 carbons and are present in crude oil. Naphthene structure is desired, for instance in reforming unit where aromatization increases its octane number.

2.5.2 Olefins

Olefins are unsaturated hydrocarbons that contain single or multiple double carbon-carbon bonds. Olefins have high octane number that promotes their presence in gasoline components. FCC cracks long olefins from crude oil to shorter gasoline boiling range hydrocarbons that are suitable in Cat gas component. However, the partial oxidation and oligomerization of them could produce high-viscosity materials, gums, that are harmful for the engines by contaminating nozzles, fuel injectors and causing sticking of the piston rings. Olefin with two double bonds is called diene that is toxic and causes harmful emissions during combustion (OICA, 2013). The FQD limits olefin content in gasoline up to 18 vol%. (Totten et al., 2003; Schobert, 2013.)

2.5.3 Aromatics

Aromatics consists of one benzene ring and they are favoured gasoline blending components, because they have high-energy density and octane number. Benzene is carcinogenic and therefore, the FQD limits it up to 1 vol%. (2009/30/EC, 2009.)
Aromatics are most complicated hydrocarbons to handle in the hydrotreating and desulphurization units, because their stable structure (Totten et al., 2003). Typically, crude oil contains aromatics between 10 to 50% and their limit in gasoline blends is 35 vol% (2009/30/EC, 2009). Lighter fractions contain unsubstituted aromatics such as benzene, while in heavier fractions contain aromatics with alkyl substituents or cycloalkane ring such as meta-xylene or cyclohexylbenzene. Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene are harmful for SI- engine, because they form soot and smoke (Kroyan, 2018; Schobert, 2013). Moreover, the incomplete combustion of aromatics causes high maintenance cost of equipment and decreases the air quality (Totten et al., 2003).

2.6 Properties of gasoline blends

The different hydrocarbon structure in gasoline blending components influences on the properties of gasoline. However, blends need to meet the requirements of law and standards always. The hydrocarbon structure of blending components varies depending on feedstock such as different crude oils or renewable raw materials. For instance, the use of oxygenates as gasoline blending components provides more functionality to gasoline and thus, generates new properties for it such as polarity. This section presents the most important properties of gasoline blends and their influence on the performance of gasoline.

2.6.1 Octane number

There is a property in gasoline that describes its ability to persist the compression without autoignition, octane number. Normally, the spark plug ignites air-fuel mixture, while pressure and induced heat in the cylinder cause spontaneous combustion of air-fuel mixture that is called knocking. Knocking occurs when these two combustion reactions occur in the cylinder simultaneously and their flame fronts hit. (Owen and Coley, 1995.) The short, transient knocking is not dangerous, but continuous one could damage the pistons and spark plug electrodes (Neste, 2015).
The autoignition of gasoline is the reason for knocking, while the pre-ignition is normally reason for so called super-knock phenomenon. Glowing particles such as small exhaust gas deposits in the combustion chamber ignite air fuel-mixture in the early stage of piston stroke that causes damages on the engine parts. The hot surface inside the cylinder accelerates the ignition of glowing particles and increases the probability of pre-ignition. Pre-ignition is normally noticed only at high loads in the presence of high temperature and pressure. (Budak et al., 2016; Neste, 2015.)
Octane number is divided into two different numbers RON and MON that are measured in the different test conditions. Usually, RON is the number that is present on the gas station in EU, while the gas stations apply the Anti Knock Index (AKI) in the USA. (Totten et al., 2003.) Today, the FQD requires the RON to be 95 and MON 85.

2.6.2 Volatility

The volatility is an important parameter to define the distillation characteristics of gasoline and moreover, the boiling range of hydrocarbons controls the proper operation of the engine during start-up and warm-up (Totten et al., 2003). The temperature of the environment has also a significant influence on the volatility by controlling it according to the temperature fluctuations (Kroyan, 2018). The higher vapour pressure compounds are called volatiles such as butane.
The vapor-to-liquid (V/L) ratio describes the probability of fuel to vaporize in automotive engine fuel systems. The high vapor pressure is specially needed in the winter to evaporate enough vaporized gasoline to ignite. That is called cold-start performance, while its opposite is the vapor lock that occurs when gasoline evaporates untimely before it even reaches the engine. In the hot summer days, the vapour lock might cause very high vapor pressure to gasoline and its consequence is the shutdown of engine until it cools enough. (Schobert, 2013.) The EN 228 standard has the vapor-lock protection measure, Vapour Lock Index (VLI), that defines its maximum value. The purpose of vapour-lock protection is to predict gasoline hot-weather performance of vehicles setting the maximum limit for VLI using vapour pressure and E70 values that Equation 4 defines shows.

$$VLI = VP * 10 + 7 * E70 \quad (4)$$

, where VP is the vapour pressure of gasoline and E70 describes the vaporized amount of gasoline at 70 °C.

The challenge of refiners is to blend right components to produce enough volatile gasoline. The one solution is to shift the boiling points of distillation fractions or adding the high vapour pressure blending components such as butane to control the vapor pressure of gasoline seasonally. There is still drawback in high vapor pressure of gasoline, because it increases smog formation that adds the air pollution. (Schobert, 2013.)

2.6.3 Heating value

The heating value is expressed by two ways, higher heating value (HHV) and LHV. The latter usually describes the heating value of gasoline, because the vaporization heat of water from gasoline combustion product is not possible to collect by condensation. The heating value for gasoline describes also its energy density that is impressed by the heat of combustion per unit volume. The expression is per volume, because the car is fuelled depending the volume of tank, not mass of it. (Schobert, 2013.) The LHV of gasoline is 32 MJ/l compared to possible future gasoline components such as 2,5-dimethylfuran (DMF), ethanol and n-butanol, the LHVs are 30 MJ/l, 21 MJ/l and 27 MJ/l. (Neste, 2015; Qian et al., 2015.)
In the investigation of gasoline components and the chemistry of them is important to focus on the carbon-hydrogen relation, since hydrogen has almost four times higher heating value than carbon. Therefore, better components for gasoline production have low amount of carbon and high hydrogen. They can offer higher energy with less amount of fuel. Moreover, the relation between carbon and hydrogen is an important factor to decrease CO2 emissions of gasoline combustion. The 2% reduction of carbon content in fuel decreases CO2 emissions by 5% that is a remarkable reduction considering emissions from transportation. (Mikkonen and Nuottimäki, 2019.)

2.6.4 Toxicity

Usually, the investigation of harmful effects of gasoline focuses on its emissions. In addition to it, the development of new gasoline blending components need to consider the land use and toxicity, especially 2nd generation feedstocks could have toxicological problems (Heger et al., 2016). For instance, DMF is one of 2nd generation feedstock that needs more research to recognize its possible health hazards and toxicology (Qian et al., 2015).
The toxicity of biofuels is a problem for the environment and, also for the human health at the manufacturing and distribution stages. Otherwise the hazards of fossil fuels, the

hazard issues of biofuels are not familiar yet. “Green Toxicology” defines the hazards of biofuels at development stages such as the contamination of water resources and soil organisms, toxicity for human genome and the inhalation problems. The research needs to focus on these hazards and their evaluation is essential before the large-scale production and their arrival into the ecologic system. (Heger et al., 2016.)
Heger et al. investigated toxicity of biofuels compared to fossil diesel in the aquatic environment. In the study were investigated several biofuels from which 2-methyltetrahydrofuran, 3-methyltetrahydrofuran and 2-butanone showed to be the least toxic. Furthermore, the most toxic biofuel candidates, 1-octanol and 2-methylfuran were less toxic than fossil diesel. The molecular structure of biomass-derived fuels influences on the differences between toxicity of biofuels. (Heger et al., 2016.)
The FQD guides gasoline blending with the limits such as aromatic and oxygenate content. These same limits concern also biofuels and therefore, they cannot contain currently more than 3.7 wt% of oxygen. (2009/30/EC, 2009.) However, some changes or additions might need to be added to the directive due to increased biofuels production in the future.

2.6.5 Oxygen content

2.7 or 3.7 wt% are the limits to the oxygen content of gasoline that the EN 228 sets. Lower oxygen content is defined, because the operability of the old vehicles cannot be secured with gasoline that has higher oxygen content. There might be the deletion of the 2.7 wt% content in the future when the old vehicles diminish, and it could even increase. There are some advantages in higher oxygen content such as

- its combustion with lower flame temperature reduces the heat lost,
- large production of combustion products and higher cylinder pressure,
- higher RON that allows larger compression ratio of the engine and
- providing more renewable gasoline. (Owen and Coley, 1995.)

2.6.6 Sensitivity

The term sensitivity describes the difference between RON and MON. In the older engines lower sensitivity is favoured, while the modern engines, particularly downsized boosted engines, favour high sensitivity and RON today. Therefore, sensitivity might be a significant property of gasoline that needs to concern in the comparison of gasoline blending components in the future. Paraffins have low sensitivity compared to olefins and aromatics, while ethanol has even higher that boosts its blending with gasoline. (Boot et al., 2017; Farrell et al., 2019; Ratcliff et al., 2018.)

3 Blending optimization

Blending is a mix of different strategies such as inventories, operability of refinery, economy targets and directives. The importance to follow different blending strategies helps to produce gasoline blends that have the high quality. The two main tasks of blending are the design of its timetable and the formation of blend. The properties of blending components such as type of hydrocarbons, dry vapor pressure equivalent (DVPE), RON, MON and LHV influence on final gasoline product. The target of blending is to mix these components to form a blend that combines their best properties. (Oduola and Iyaomolere, 2015.)

Gasoline production is 60-70% of the profits of the refineries in the USA, while European countries have the overproduction of gasoline. The reason for the overproduction is the options to produce gasoline from lighter crude oils or shale oil. However, surplus gasoline can be sold to the USA and South America and thus, the cutting of gasoline production is not necessary. (Oduola and Iyaomolere, 2015; Sinervä, 2018.) Moreover, the registration of the new gasoline cars increased 6.5 percentage unit in 2018 and it covers now 56.7% of all new registered cars in Europe. This is a proof that gasoline has the demand also in the future (Kortelainen, 2019). New registrations offer also the possibility to produce renewable gasoline that could increase gasoline product selection in refineries and decrease CO2 emissions.

In the next section is presented linear blending that is the easiest method to estimate properties of final gasoline blend. While non-linear blending provides challenges for the estimation of blend properties, for instance RON and MON. The section 3.2 explains the reasons for the non-linearity and tries to search the differences among different blending components with the help of their hydrocarbon structure and oxygenates. Also, the vapour pressure blending is non-linear that is showed in the section 3.3 for ethanol and gasoline blends.

3.1 Linear gasoline blending

Co-optima team researches linear blending among different properties of gasoline blends. They present the calculation of the heat of vaporization (HOV) for gasoline blend assuming HOV blending approximately linear that Equation 6 shows.

$$HOV(gasoline\ blend) = x1 * HOV(blending\ component\ 1) + x2 * (blending\ component\ 2) + \quad \ldots xn * (blending\ component\ n) \qquad (6)$$

, where xn is a molar or volume fraction of gasoline component and HOV (blending component n) is heat of vaporization of component.

Knowing the molar ratios of blending components and their HOVs the final HOV of gasoline blend can be calculated based on Equation 6 (Farrell et al., 2019). Equation

6 provides the principle for calculation also other linear gasoline properties such as the amount of aromatics, olefins and paraffins.
However, the mixing of gasoline blending components to produce gasoline blend with high octane number is not linear for all its properties. The RON, MON and DVPE do not blend linearly that causes challenges for the estimation the final properties of gasoline. However, Ghosh et al. discovered linear octane blending among the similar hydrocarbon composition of blending components such as paraffins blends linearly with other paraffins and olefins with other olefins. What is interesting to notice is linear blending of naphthenes and olefins that this study shows. (Ghosh et al., 2006.) However, gasoline components consist often more than one hydrocarbon group that poses more complex compositions that linear octane blending cannot anymore explain.

3.2 Non-linear gasoline blending-Synergistic and antagonistic octane blending

Blending of two chemically different gasoline components together could produce gasoline which octane number differs significantly from the octane numbers of individual gasoline components. The identification of this phenomenon is extremely important for the estimation of the octane number of gasoline. There are two terms that describe the non-linear octane blending: synergism and antagonism. The synergism provides higher octane number than the linear octane blending assumes, while the antagonism provides lower one. In Figure 3 is presented the difference between synergistic, linear and antagonistic octane blending.

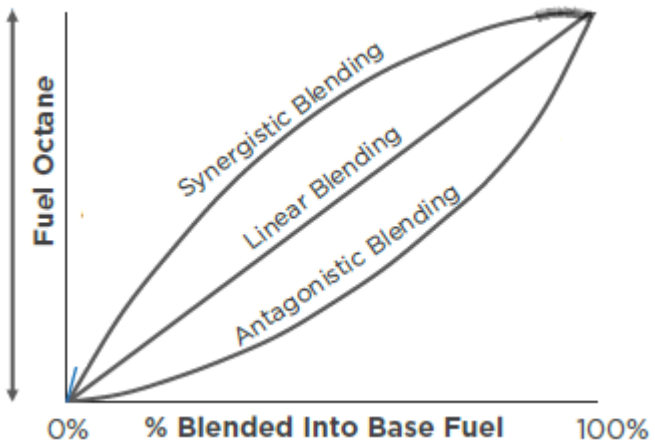

Figure 3. The synergistic and antagonistic behaviour of fuel octane blending ((Farrell et al., 2019), [Modified 23.9.2019]).

The octane number of different alkylates and isomerates has been noticed to blend synergistic. While reformates have been noticed to blend antagonistically and therefore, the octane number of gasoline blend is lower than expected according to the linear blending. (Boot et al., 2017.) Ghosh et al. noticed also octane blending of paraffins and olefins to be non-linear but could not prove is it synergistic or antagonistic (Ghosh et al., 2006). In addition to the hydrocarbons, Co-optima research team investigated the blending of oxygenates such as esters with gasoline. In the study, they noticed that it is antagonistic otherwise the blending of gasoline with furans and cyclic ketones is synergistic. (Farrell et al., 2019.)

Ethanol boosts the octane number of gasoline blend depending on the hydrocarbon structure of other blending components in the blend. It blends with n-paraffins, iso-paraffins and olefins synergistically, while with aromatics antagonistically. However, short side chains like methyl shift blending between ethanol and aromatics toward linear and even synergistic, but longer side chains such as propyl group or even longer might keep the blending antagonistic. Longer paraffins add the synergistic phenomena in ethanol blending, for instance comparing iso-octane and iso-heptane, is the synergy greater with iso-octane-ethanol blend. Similarly, longer n-paraffins increase synergistic phenomenon compared to shorter ones. (Badra et al., 2017; Boot et al., 2017.) Farrell et al. studied non-linear octane blending and found out phenomenon that improves the RON even more than synergistic blending. It is called hyper-boosting phenomenon that Farrell et al. noticed during blending prenol with gasoline blend. The hyper-boosting phenomenon produces higher RON than either of blended components have. Normally, the RON of final blend cannot be higher than its blending components individually have, but in the case of prenol and gasoline it is. That phenomenon could increase the utilization of alcohols like prenol to increase the RON of gasoline even though the RONs of blending components are not initially high. (Farrell et al., 2019.)

3.2.1 Carbon-carbon bonds, reactivity and reaction rate

Boot et al. has investigated the influence of the carbon-carbon bonds, reactivity and reaction rate on RON, to explain why it differs among different hydrocarbon types. They noticed longer paraffins to be more reactive, because they have more possible reaction sites. The longer chain causes short ignition delay times and the better cetane number, while the RON decreases and the probability of knocking in the engines increases. (Ghosh et al., 2006; Boot et al., 2017.)

Cyclic and straight chain paraffins have different RONs even though the carbon number is same, for instance six carbon hydrocarbons, n-hexane and cyclohexane, have RONs 25 and 83. (Boot et al., 2017.) Compared paraffins to same carbon number cyclic paraffins, is their reactivity higher. During hydrogen abstraction reaction small radical such as OH removes H atom from n-paraffin molecule and forms alkyl radicals, while the hydrogen abstraction of cycloalkanes form cycloalkyl radicals. That reaction

needs less energy in the case of n-paraffins than cycloparaffins and therefore, the formation of alkyl radicals is more probable. Those radicals react with oxygen and produce less conjugated compounds that have lower RON compared to the products form the reaction of same size cycloalkyl radicals and oxygen. This reaction produces more conjugated compounds with high RON that resists autoignition reactions in the low temperatures. (Battin-Leclerc, 2008.)

Boot et al. investigated also the structure of olefins to explain their high RONs. They noticed that double bonds increase the octane number, because they create delocalized unpaired electrons that increase stability of olefins (Boot et al., 2017). Moreover, De Bruycker et al. investigated the influence of carbon-carbon double bond on the radical formation. They noticed the C-H bond of carbon atom that is in the **α**-position to the C-C double bond is weak and therefore, its scission leads resonantly stabilized radicals. In addition, the C-C bond between **α**- and **β** -positions is weak, and its scission product is also a resonantly stable radical that does not probable react with oxygen. Because these compounds have lower reactivity, they also have high RONs. (De Bruycker et al., 2016.) Figure 4 shows the positions of carbons to point those that are involved in the formation of resonantly stabilized radicals.

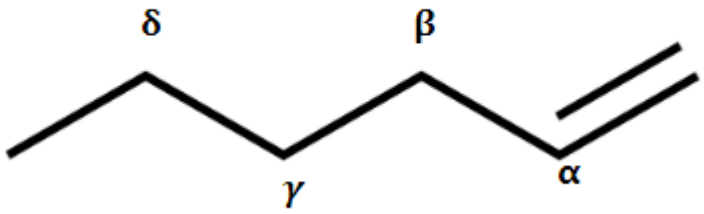

Figure 4. The nomination of carbons in olefin structure ((ChemSpider, 2019b), [Modified 30.8.2019]).

Bounaceur et al. investigated the influence of the position of double bond on the autoignition and measured the RONs of 1-hexene, 2-hexene and 3-hexene, 76.4, 92.7 and 94. The bond dissociation energy (BDE) indicates how strong the bond between carbons or carbon and hydrogen is in hydrocarbon molecule. The position of double bond in the carbon chain influences on the BDE between carbons and hydrogens even increasing or decreasing it. The C-H bonds that have low BDE are more reactive, easier to break and have low RON. (Bounaceur et al., 2009; Boot et al., 2017.) The lowest BDE of C-H bond has tertiary bonds (T), then secondary bonds (S) and the highest has primary bonds (P) that Figure 5 illustrates.

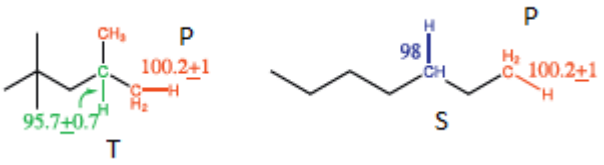

Figure 5. The primary (P), secondary (S) and tertiary (T) C-H bonds are placed in iso-octane and n-heptane ((Boot et al., 2017), [Modified 23.9.2019]).

1-Hexene has six secondary C-H bonds and three primary C-H bonds, while 2-hexene has four secondary C-H bonds and six primary C-H bonds. The lower amount of the primary bonds in 1-hexene proves its lower RON compared to 2- and 3-hexene. However, 2-hexene and 3-hexene contains equal amount of primary and secondary C-H bonds, but 3-hexene has shorter paraffinic chain length that decreases its reactivity compared to 2-hexene. Figure 6 indicates paraffin chain in olefins with the blue circles.

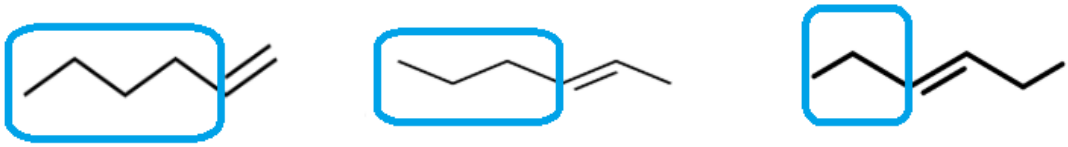

Figure 6. The hydrocarbon structure of 1-hexene, 2-hexene and 3-hexene with the blue marked paraffinic chain ((ChemSpider, 2019b; PubChem, 2019; ChemAladdin, 2019), [Modified 29.8.2019]).

Aromatics covers normally the one third of gasoline and their structure is different than paraffins and olefins, because their core is benzene ring. Aromatics are by themselves nucleophiles with high pKa value and they offer a possibility to the electrophilic substitution such as replacing H atom with radical like OH. Because of the π-bond in aromatic ring the removing of hydrogen is extremely hard and therefore, aromatics are resistant for auto-ignition at low and intermediate temperatures. Addition of long side chains into aromatics increases its reactivity in the low temperatures and decreases octane number. Toluene consists of aromatic ring and one methyl group, and xylene consists of aromatic ring with two methyl groups. Their side chains are short that boosts their octane numbers, because they form resonance stable radicals during bond scission. Benzyl is an example of these radicals that is stable radical, has low reactivity and resists the autoignition. (Boot et al., 2017.)

3.2.2 Electrophilicity

Whitmore et al. investigated the influence of molecular structure of gasoline on the RON. In the study, they noticed that electrophilicity has an influence on the RON by decreasing it as Figure 7 shows. Therefore, more nucleophilic compounds are suitable for increasing RON. (Whitmore et al., 2016.)

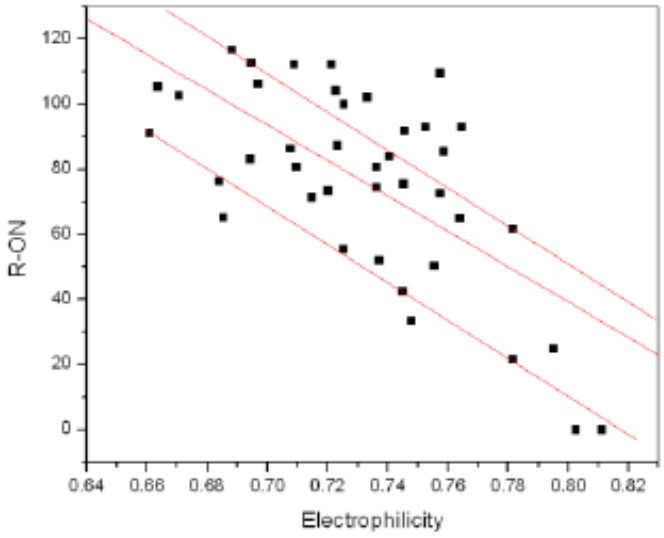

Figure 7. Electrophilic compounds decrease the RON (Whitmore et al., 2016).

De Vleeschouver et al. investigated the electrophilicity and nucleophilicity indexes of different radicals and noticed for instance higher electrophilicity of hydroxyl than benzyl radical (De Vleeschouwer et al., 2007). This proves benzyl to be more stable compared to hydroxyl radical and, also to have higher RON. Hydrocarbons are nucleophilic compounds, because of hydrogen and carbon atoms in their structure have small electronegativity difference. While compounds that have single or double bonds to electronegative atoms such as oxygen and nitrogen, are more electrophilic. Electronegative atom reduces energy of the orbital modifying it to accept electrons and thus, produces more electrophilic compounds. Alcohols are neutral nucleophiles, while C=C bonds are nucleophilic that decrease the reactivity of aromatics and olefins. (Clayden and Clayden, 2001.)

3.2.3 Chain branching

The isomerization of paraffins increases their RON, because it adds branching to them. Smaller surface area of isoparaffins than n-paraffins explains the difference in their RONs: Higher surface area forms reactive radicals during bimolecular initiation reaction, where oxygen and gasoline molecules interact via London-force attractions.

These forces diminish during reaction between isoparaffins and oxygen that forms more stable radicals which will auto-ignite less probable. (Schobert, 2013.)
Ghosh et al. researched the influence of chain branching on the gasoline octane number and observed that the RON varies a lot depending on the amount of side chains in the carbon backbone. For instance, comparing 2-methylheptane and 2,2,3-trimethylpentane, the RONs are 20 and 110, even though they have equal amount of carbons. 2,2,3-trimethylpentane has low reaction rate, because it has smaller paraffinic chain length and less existing reaction sites compared to 2-methylpentane. (Ghosh et al., 2006.)
There has been noticed to be an effect of position of the branch to the octane number in isoparaffins. The side chain in the centre of the carbon backbone improves the octane numbers, because the paraffin chain length decreases. As it was proved before, shorter paraffin chain length has higher RON and therefore, more centric side chains in the carbon backbone are preferred. (Boot et al., 2017.) Figure 8 concludes the impacts of branching and number of carbons on both octane numbers, RON and MON.

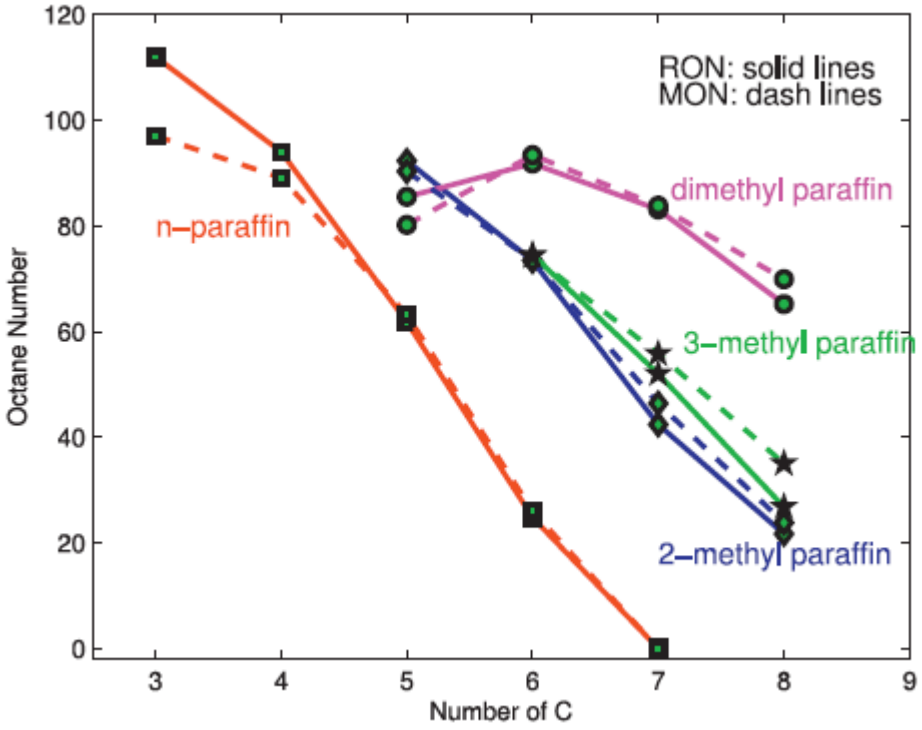

Figure 8. More branched and shorter hydrocarbons have higher RON and MON (Boot et al., 2017).

What stands out in Figure 8 is the reduction of octane numbers when the number of carbons increases. Also, Figure 8 shows that isoparaffins have higher-octane number compared to same carbon number n-paraffins. Dimethyl-propane is the only exception in Figure 8 that does not behave according the trend. It has lower RON and MON than dimethyl-butane, because methyl groups are both in same carbon atom that produces quaternary carbon in hydrocarbon. This carbon is more reactive and increases the reactivity of the whole hydrocarbon that decreases its octane numbers.

3.2.4 Oxygenates

Ethanol consists of one OH-group that affects to the BDE of the bonds between carbon and hydrogen. It decreases the reactivity of the carbon chain compared to alkanes with the same chain length. (De Bruycker et al., 2016.) Koivisto et al. noticed that secondary OH-group decreases the BDE of C-H bond in **α**-carbon atom (nearest C-atom of OH-group) and increases the BDE of C-H bond next to **α**-carbon and the other secondary carbon atoms by hindering the cleavage of hydrogen atoms from them. Figure 9 shows with dash lines which C-H bonds have higher BDE, because of the secondary OH-group. (Koivisto et al., 2015)

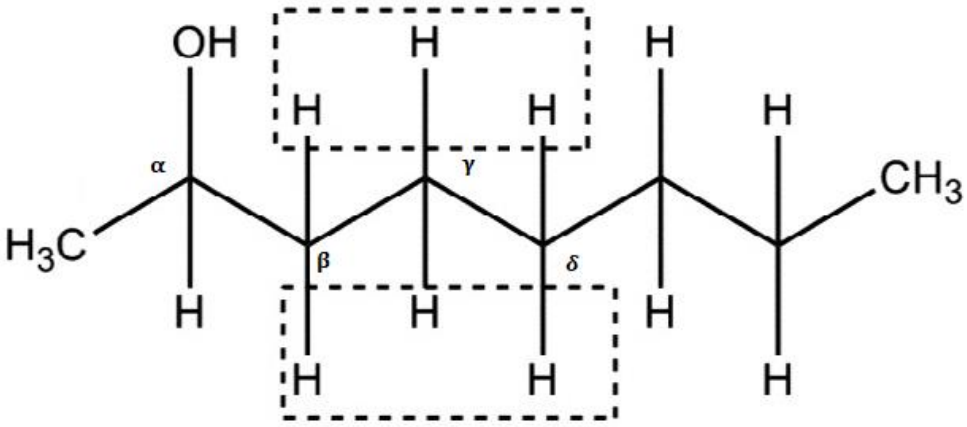

Figure 9. The secondary OH-group increases the BDE of β-carbon atom that reduces its reactivity ((Koivisto et al., 2015), [Modified 6.8.2019]).

Secondary OH-group causes difficulties for H-abstraction from secondary alcohols and decreases the rate of radical formation. Lower amount of free hydrogen radicals prolongs the ignition delay time for next reactions that increases the octane number of these compounds. (Koivisto et al., 2015.)

3.3 Vapour pressure blending

Concave organisation studied the effect of ethanol to the vapour pressure of gasoline and noticed that ethanol increases it significantly when it is added 5 vol%. However, in higher ethanol concentrations the vapour pressure starts to decrease. Concave organisation studied 60 different base fuels that have different ether, aromatic and olefin compositions. They added ethanol from 0-25% to these base fuels to find out how it affects to the DVPE, density and distillation curves. The input data also includes the

DVPE of base fuel, its E70 and E100 values. In Figure 10, is showed the influence of ethanol on the DVPE of gasoline when their composition varies. (Rose, 2009.)

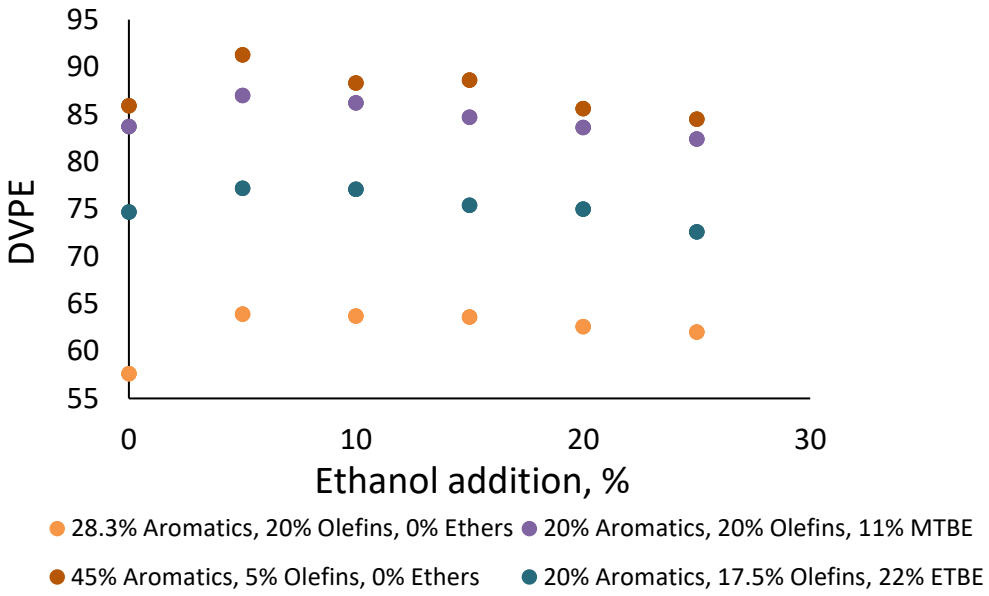

Figure 10. The 5% addition of ethanol could increase the DVPE rapidly (Rose, 2009).

What stands out in Figure 10 is the rapid rise in the DVPE with addition of 5% ethanol to gasoline blends without other oxygenates as orange and red curves present. There has been studied the influence of ethanol to the DVPE of gasoline in some studies, for instance Da Silva et al. studied gasoline blend structure to find out how hydrocarbon groups influence on the DVPE when they added ethanol, MTBE or ETBE into it. The study proved that adding 5% ethanol into blend with high aromatic ratio the DVPE increases less than in paraffinic and naphthenic blend. The formation of ethanol azeotropes with aromatics causes its lower rise. (Da Silva et al., 2005.) Figure 10 shows the same increase of the DVPE with 5% ethanol addition, but then it declines, because the formation of azeotropes begins between ethanol and aromatics. All blends in the Concawe study have high amount of aromatics and therefore, the influence of paraffins on the DVPE of gasoline blend is hard to recognize.

Bays et al. investigated the behaviour of DVPE of gasoline blend with higher ethanol concentrations. They explained it with the forces between molecules in gasoline blend and ethanol. There are mainly van der Waal' forces in gasoline blend when it does not contain ethanol. While, the 10 mol% addition of ethanol into it causes a disruption to these forces. Adding even more ethanol, hydrogen starts to form bonds with oxygen of ethanol molecules that forms small clusters which could increase DVPE. The addition of ethanol over 20 mol% causes the formation of the wider hydrogen bonding network that decreases the small ethanol clusters but increases the larger hydrogen-bonding networks that might decrease DVPE. (Bays et al., 2019.)

Da Silva et al. noticed that ETBE in high aromatic blend decreases DVPE linearly when ethanol content increases, while the trend is opposite in paraffinic and naphthenic blend, in which the additions of ETBE increase DVPE. Whereas, MTBE increases the DVPE in both blends and even more in gasoline blend with low aromatic content. (Da Silva et al., 2005.)

4 Renewable feedstocks for the future production of gasoline

27% of the CO_2 emissions in EU are caused by transportation and 41% of these emissions produces passenger cars (Transport and environment, 2018). These numbers show that there is a huge need for the development of more sustainable fuels to decrease those emissions. To decrease the carbon footprint of fuels, refineries should start to utilize renewable raw materials instead of fossil ones. Moreover, the price of crude oil increases that could increase the costs of the refining and decrease its profitability (Masum et al., 2015). There are still challenges to produce profitable gasoline from renewable feedstocks in the refineries and the yield of the conversion routes affect strongly to future gasoline production. For instance, the 2nd generation feedstock, forest residue, needs the pre-treatment before its utilization (Naik et al., 2010). These pre-treatment methods are energy consuming processes that decreases their utilization (Dutta et al., 2014).
Renewable feedstocks are divided into four generation that all have their own advantages and disadvantages. This chapter lists the different generations and provides three renewable compound examples that are possible feedstocks for the more sustainable gasoline production.

4.1 From the 1st generation biofuels to electrobiofuels

1st generation: Food and plant based and 2nd generation: Residue and waste based

The feedstocks for first generation biofuels are oilseed, corn, wheat and sugarcane that compete against food production and thus, they are not reasonable alternatives to produce biofuels. The competition for land use against food production increases food prices and, also reduces the available food for animals. The utilizing of the 1st generation feedstocks to produce biofuels could reduce emissions like CO, particulate matters and smoke emissions. However, the direct use of vegetable oils for instance in the diesel engines contaminates them with wax and gum. (Dutta et al., 2014.)

There are many drawbacks in the utilization of 1st generation feedstocks, but their use is also acceptable, if it is done in the sustainable way. To verify the responsibility of renewable products is to utilize only the certificated feedstocks. It ensures that the cultivation does not occur in the forbidden areas such as rainforests, biodiversity is preserved, and the production of feedstocks does not disrupt the human rights. (Neste, 2019c.)

2nd generation biofuels do not compete against the food production and their raw materials are for instance lignocellulosic feedstocks such as cereal straw and forest residues. Ethanol is also produced from the 2nd generation feedstocks such as forest residues and organic part of municipal waste by fermentation. This production does not consume the environment and has not impact on the food production like the utilization of 1st generation feedstocks have. (Dutta et al., 2014.) Moreover, possible feedstocks for the production 2nd generation biofuels are plastic wastes that are concerned potential raw materials for the fuel production. The use of plastics has increased 5% every year since 1990, and the highest users of them are the packing materials, households, agriculture and cars. The plastic waste is divided into the municipal and industrial waste from which the industrial waste is more homogenous and, also less contaminated. (Kunwar et al., 2016.)

Plastics consist of hydrocarbons, they have not oxygen that provides them high heating value and moreover, they are non-acidic and non-corrosive raw materials. There are several factors in the plastic wastes that influence on their utilization in the gasoline production such as feed composition, particle size and catalysts. The thermally degradation of plastic wastes increases its popularity, because it could produce smaller hydrocarbon chains that are possible raw materials for gasoline. It is possible to convert plastics to fuels with or without catalyst, pyrolysis of plastics or conversion of polyvinyl chloride (PVC). However, the main problem of PVC in the fuel applications is its large production of hydrogen chloride (HCl). Its removal has been researched a lot and the possible methods are applying adsorbents after pyrolysis or its removal already before pyrolysis. (Kunwar et al., 2016.)

There are still challenges in the plastic pyrolysis such as a high viscosity and a low thermal conductivity of plastics. The reduction of viscosity is an important part of the plastics modification to fuels in which vacuum gas oil or waste oils can provide help, because their addition into stream decreases the viscosity. Kunwar et al. researched the mixture of low-density polyethylene plastics and lubricant oil for the fuel production using two different catalysts. They noticed that change of catalyst produces different hydrocarbons, aromatics and olefins that are viable hydrocarbons in gasoline blending components. (Kunwar et al., 2016; Ratnasari et al., 2017.)

There are two possible ways, esterification or hydrotreating of vegetable oils (HVO) in the production of biofuels from 1st and 2nd generation feedstocks. The name HVO is misleading, because in general, it hydrotreats wastes and residues, not only vegetable oils. Difference between these two processes is the composition of the end-product that in the case of esterification is fatty acid methyl ester (FAME) that contains oxygen,

while HVO process produces oxygen free paraffinic biofuel that Figure 11 presents. (Neste, 2016.)

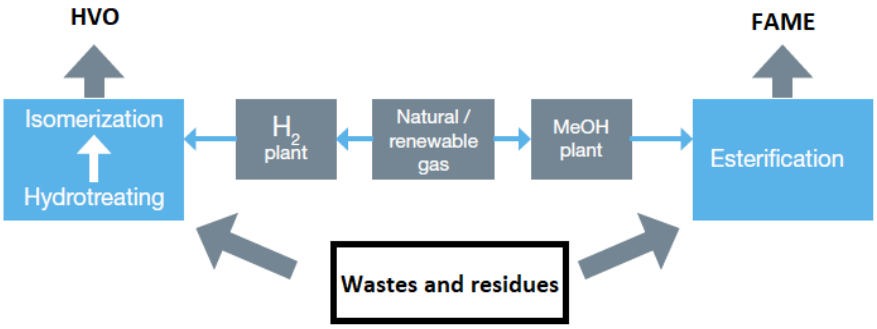

Figure 11. The esterification of wastes and residues produces FAME, while the hydrotreating produces HVO ((Neste, 2016), [Modified 17.9.2019]).

The esterification produces biodiesel, FAME, otherwise HVO produces renewable diesel that Figure 11 illustrates. Due to oxygen in biodiesel, it is polar compound, has lower LHV than renewable diesel and its density is higher. (Neste, 2016.)
Neste uses its developed "Next Generation Biomass To Liquid" (NEXBTL) technology to produce its own renewable diesel product Neste MY Renewable Diesel™ that uses wastes and residues as raw materials. The technology can utilize multiple low-quality raw materials without losing the quality of renewable diesel. The NEXBTL applies hydrogen for removing oxygen from triglyceride vegetable oil molecules and then hydrogen divides triglyceride into the three chains that are chemically similar as conventional diesel fuel components. There is also included isomerization unit in the NEXBTL technology to improve cold properties of renewable diesel like the cloud point. (Neste, 2016.)
Because Neste MY Renewable Diesel™ is paraffinic, it meets the EN 15940 standard for paraffinic diesel that also allows the use of FAME in diesel blends, but Neste MY Renewable Diesel™ does not contain it. In addition, it meets completely the requirement of the European diesel fuel standard EN 590, except the density, that is below lower limits. However, Neste MY Renewable Diesel™ can be blended into fossil diesel according to EN 590 within a range of density. (Neste, 2016.)

3rd generation: Algal based

Algae are aquatic, photosynthetic microorganisms that exist in the marine environments and in fresh water. They are promising feedstocks for 3rd generation biofuels, because they can be cultivated in the low lagoons or ponds and therefore, they do not compete against the food production. After the cultivation, biomass is harvested from the lagoons and the oil extraction, transesterification, gasification or biochemical processes upgrade it to biofuels. The production of algal biofuel is possible throughout

the year, but it is dependent of light irritation and its oil yield is in the same range than from rich oilseed crops. (Dutta et al., 2014 ¸ Lü et al., 2011.)

4th generation: Solar biofuels-photobiological fuels and electrobiofuels

Typical 4th generation biofuels are biodiesel, bioethanol, syngas, biobutanol and bio-hydrogen that are considered as clean and environmentally suitable fuels (Dutta et al., 2014; Lü et al., 2011). Their feedstock is solar energy that is by photobiological or photochemical reactions converted into biofuels using endless and cheap feedstocks: water and CO_2 as substrates. The three ways to produce 4th generation biofuels are:

- By photosynthetic micro-organisms,
- by combining photovoltaics and microbiological fuel production or
- by synthetic cell factories or organelles. (Aro, 2016.)

There is difference in the production of 4thgeneration biofuels and current biomass feedstock biofuels, because former applies of cells that emit the product out of the cell. It could avoid the costly fermentation that is common in the production of biomass - based biofuels. Also, the operational costs could decrease in the production of 4th generation biofuel compared to the conventional methods, because the amount of the process steps decreases. (Dutta et al., 2014; Lü et al., 2011.)

4th generation fuels are promising alternatives for fossil fuels, but there are still technical risks in their production and, more knowledge is needed. Table 3 summarizes the advantages and challenges of different generation biofuels.

Table 3. The advantages and challenges of biofuels produced from different generation feedstocks (Dutta et al., 2014).

Generation	Advantages	Challenges
1st: Food and plant	Simple conversion routes	Competition with food production
	GHG savings	Low yield depends on the source
2nd: Residue and waste	Utilize wastes	Expensive pre-treatment of lignocellulose
	No food crop competition	Need of advanced technology for biomass conversion
	GHG savings	
3rd: Algal	No food crop competition	Energy consuming cultivation
	Simple to cultivate	Low lipid content of biomass
	Can utilize waste water	
4th: CO_2	High yield	Early stage
	No need for biomass	Expensive photo-bioreactor
	CO2 extraction	

4.2 The possible feedstocks to produce renewable gasoline

For substituting crude oil in the future is necessary to research the renewable feedstocks. There might be challenges in these feedstocks such as oxygen that has an influence on the reactions and the catalysts in the conventional upgrading units (Masum et al., 2015). Qian et al. listed three main criteria to produce gasoline in the future:

- carbon is obtained from the atmosphere,
- the combustion of gasoline must be effective without engine modifications and
- production of gasoline is economic. (Qian et al., 2015.)

This section of the thesis presents the renewable feedstocks to the existing upgrading units in the refineries that they could modify into gasoline blending components. Some feedstocks are already possible to blend gasoline without upgrading.

Furans

Furans are heterocyclic organic compounds which can be produced from biomass. For instance, methyl- and dimethylfurans have high octane-number and are possible blending components. They also reduce the acetaldehyde emissions of gasoline approximately 40% and formaldehyde 20% compared to fossil-based (Qian et al., 2015). However, they also produce gum that is harmful for the engines. (The U.S. Department of Energy, 2018.)

DMF has high RON and therefore, high knocking resistance, it decreases the density and DVPE of gasoline blends but increases their viscosity. Two possible process pathways to produce DMF from biomass are to pre-treat biomass and split it to glucose and fructose and then remove oxygens to form 5-hydroxymetylfurfural (HMF) that the hydrogenolysis transforms DMF. Another possible pathway it to dehydrate biomass to 5-chloromethylfurfural (CMF) and then hydrogenate it to DMF. (Qian et al., 2015.) The one fourth addition of DMF to gasoline blends could increase its thermal efficiency and decrease its consumption. (Liu et al., 2019.) However, NOx and particulate emissions might increase, because DMF has fast burning speed that causes the high temperature during combustion. DMF has higher heating value than ethanol and n-butanol, but lower compared to fossil gasoline. Its DVPE is significantly lower compared to gasoline that may cause start-up problems during winter. (Qian et al., 2015.) This master thesis investigates DMF as a potential feedstock for the upgrading units to produce renewable gasoline blending components otherwise its use straight as gasoline blending component. Figure 12 shows the reaction method to remove oxygen and double bonds from DMF.

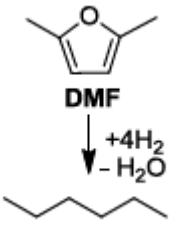

Figure 12. DMF is a potential renewable feedstock in the gasoline upgrading units and, also straight as gasoline blending component ((Sacia et al., 2015), [Modified 4.9.2019]).

The removal is called hydrodeoxygenation (HDO) that releases water when DMF reacts with four hydrogen molecules as Figure 12 presents. During the reaction also the two double bonds are hydrogenated. The final product is n-hexane that is a possible feedstock for instance into the isomerization unit. (Sacia et al., 2015.)

Ketones

Ketones are bio-derived molecules that have oxygen attached them by double bond. Their possible use as a feedstock for gasoline production requires the removal of oxygen that can be executed by the HDO method. It consists of three steps: reduction of ketones to alcohols, dehydration of alcohols to alkenes and hydrogenation of alkenes to alkanes. Figure 13 summarizes those three reaction steps to produce nonane from 5-nonanone. (Jenkins et al., 2017.)

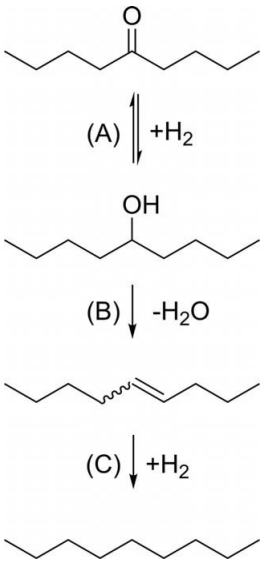

Figure 13. The HDO of 5-nonanone consists of three reaction steps (Jenkins et al., 2017).

Jenkins et al. applied supported Ni and Pd catalysts to reduce ketone to alcohol and aluminosilicate zeolite (HZSM-5) solid acid catalyst to dehydrate alkenes. The results show that the conversion of reduction is over 88% and dehydration over 99%, while

straight HDO of 5-nonanone to nonane with combination of these catalyst has 99% conversion. (Jenkins et al., 2017.) Alotaibi et al. investigated also the HDO of ketone, methyl-isobutyl ketone (MIBK), with bifunctional Pt/HZSM-5 catalyst as Figure 14 shows. Their study shows that the conversion of MIBK to 2-methylpentane is over 99%. (Alotaibi et al., 2012.)

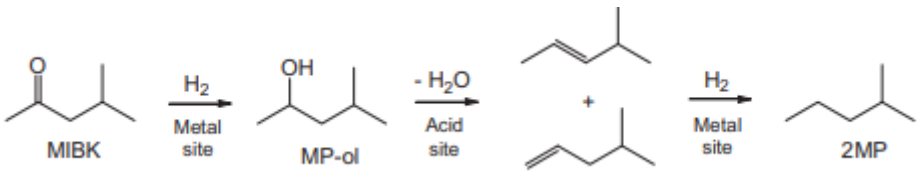

Figure 14. The production of 2-methylpentane from MIBK (Alotaibi et al., 2012).

The HDO pointed to be a viable process pathway to produce hydrocarbons from ketones that could form gasoline blending components. There have been founded 2-methylpentane in the HDO of MIBK that could be possible feedstock into isomerization unit.

Terpenes

Terpenes are organic compounds, that plants, especially softwoods produce and, also, they exist in the industrial waste streams (Tsolakis et al., 2019). They are components of essential oils of plants and flowers that perfumery and traditional medicines apply. Terpenes are hydrocarbons and therefore, do not contain oxygen that provides potential for their use as feedstocks for gasoline production. Co-optima introduced monoterpenes that are terpenes with two isoprene units that Figure 15 shows (The U.S. Department of Energy, 2018). Limonene, myrcene and α-pinene, that Figure 16 presents, are examples of monoterpenes that are possible feedstocks in the gasoline upgrading units.

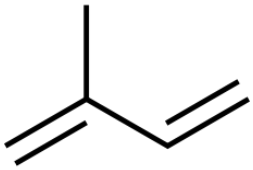

Figure 15. Isoprene unit is a building block of monoterpenes (ChemSpider, 2019c).

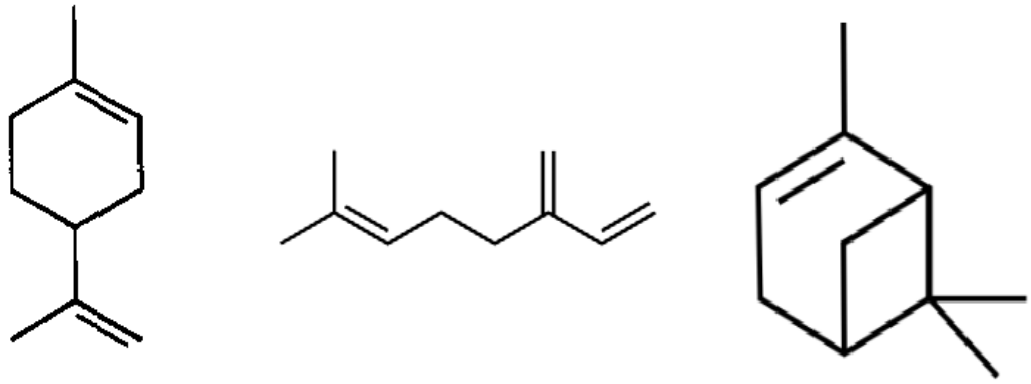

Figure 16. The structure of monoterpenes: α -limonene, myrcene and α -pinene (Weyrich and Hölderich, 1997; ChemSpider, 2019a; Tracy et al., 2009).

α-limonene, left hydrocarbon in Figure 16, is a natural terpene that is a by-product from the orange juice production and the paper industry. Figure 17 shows the reaction pathway in which double bonds are hydrogenated from α-limonene that forms p-menthane (Weyrich and Hölderich, 1997).

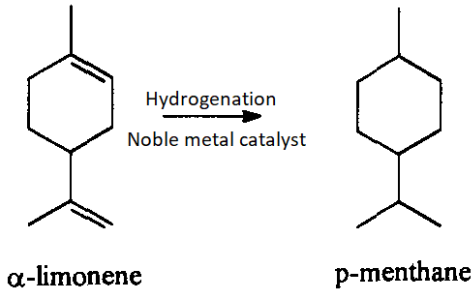

Figure 17. Hydrogenation of α-limonene to p-menthane in the presence of noble metal catalyst (Tracy et al., 2009).

Tracy et al. investigated the hydrogenation of α-limonene to p-menthane with two different noble metal catalyst, palladium supported activated carbon and platinum supported alumina pellets. The gas chromatography (GC) shown the composition of hydrogenated limonene to be 72.4 wt% of p-menthane and 25.3 wt% of m-cymene. (Tracy et al., 2009.) P-menthane is a possible feedstock for instance into reformation unit that could aromatize it.

Myrcene is polyolefinic monoterpene, in the middle of Figure 16, that appears in tree oils. Tracy et al. investigated its hydrogenation and results show that the hydrogenation produces over 84.5 wt% 2,6-dimethyloctane and under 9 wt% cyclohexane. (Tracy et al., 2009.) 2,6-dimethyloctane could be fed into the reformation unit that upgrades it into high octane gasoline blending component via cyclization and aromatization. Moreover, Tracy et al. analysed the distillation of hydrogenated myrcene and α-limonene and noticed their very high final boiling points, 363.7 and 359.8°C (Tracy

et al., 2009). The FQD limits the final boiling point on 210 °C that these monoterpenes exceed (2009/30/EC, 2009). However, the further upgrading of them could decrease it by shorten carbon chain length.

α-pinene is monoterpene and by-product from Kraft pulping process in the paper mills. It is a natural product that medicine and fuel industry utilize, but its separation from the trees is still hard and inefficient. (Yang et al., 2013.) Roberge et al. investigated crude sulphate turpentine (CST), the most used feedstock for α-pinene to the production of p-cymene. The concentration of α-pinene in CST varies depending on the region, tree species and the season. The distillation and desulphurization units could remove α-pinene from CST that also exist in the most oil refineries (Erman and Kane, 2008). Roberge et al. found out three other possible products beside p-cymene that the modification of α-pinene could produce and they are presented in Figure 18. (Roberge et al., 2001.)

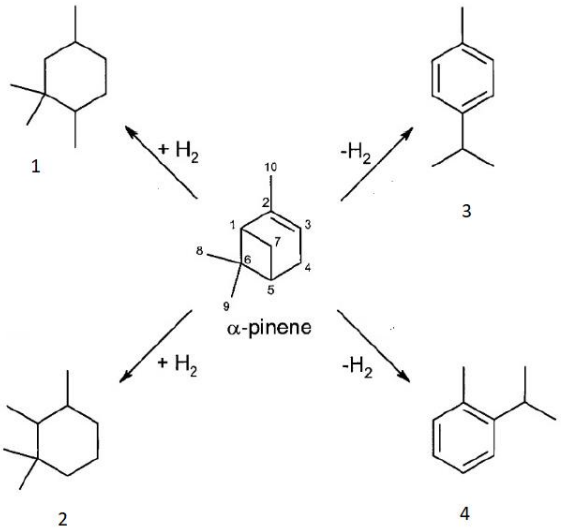

Figure 18. The four possible compounds from the hydrogenation and dehydrogenation of α-pinene (Roberge et al., 2001).

Roberge et al. applied Pd supported on high surface area carriers -catalyst in the dehydrogenation reaction of α-pinene (Roberge et al., 2001). In Figure 18 are presented results from the hydrogenation of α-pinene that produces side products 1 and 2. Those products are possible feedstocks for the gasoline upgrading units.

In addition to monoterpene, Tracy et al. have studied production of gasoline from triterpene, squalene, which structure Figure 19 presents (Tracy et al., 2011).

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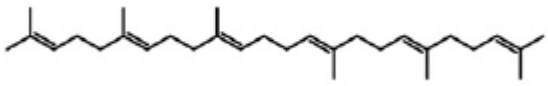

Figure 19. The structure of squalene, triterpene, is an optimal feedstock for the gasoline production (Tracy et al., 2011).

There are six double bonds in Squalene and its carbon chain is 24 carbon long which includes six methyl groups as Figure 19 presents. Algae, especially microalgae produce these long-chain molecules that are possible to exploit as feedstocks for gasoline production, especially for the fluidized catalytic cracking. Also genetically modified *E. coli* bacteria is possible raw material which from squalene can be extracted. (Tracy et al., 2011.)

5 Collection of the database

The purpose of the thesis is to collect property database for gasoline blending components that contains input data for the future gasoline blending calculator. The data is from the daily gasoline analysis that have been measured in the laboratories in Neste Porvoo refinery which the Neste laboratory management system (LIMS) reports. The time interval for the gasoline analysis is two and half years, but the database has also older analysis to ensure the data from components that are more seldom analysed. The database is provided only for the use of Neste and the Digifuels project.
With the help of the database is explained how components blend together and provided the advices to the selection of viable renewable feedstocks for the upgrading units to produce existing gasoline blending components. In this chapter are introduced the collecting process of the database and the properties of gasoline that it includes.

5.1 PONA analysis

To examine the chemical structure of hydrocarbon mixtures is applied the PONA analysis that is a GC-method. The word PONA is abbreviation from paraffins, olefins, naphthenes and aromatics, but it also offers detail chemical structure of oxygenates. During the analysis fractions are separated and quantitated from gasoline blending components with GC to classify them according to the hydrocarbon group, carbon number and hydrocarbon or oxygenates name. (Shimadzu Global analytical and measuring instruments, 2019.)
There are PONA analyses in the Neste LIMS that this thesis utilizes to examine the structure of gasoline blending components. These analyses list chemical compounds and identifies their quantities from gasoline blending components. Those analysed hydrocarbon groups are n- and isoparaffins, paraffin-and olefin-naphthenes, olefins, aromatics and oxygenates.

5.2 The defined properties of gasoline blending components

In the database is reported properties for the gasoline blending components that this section presents below detailed.

- Density

The LIMS analysis provides densities of gasoline blending components that are reported as median values in database in the unit kg/m^3 from the earlier specified time frame.

- Hydrocarbons

In the database, hydrocarbons are presented as the volumetric percent of each gasoline components.

- Paraffins

There are paraffins of gasoline blending components in the database that are divided into n-and isoparaffins that are results of the LIMS analysis.

- Olefins

The content of olefins is from the LIMS analyses for all gasoline blending components as median values.

- Aromatics

From the LIMS analyses are also obtained the content of aromatics for all gasoline components as median values.

- Naphthenes

In the LIMS is provided naphthene contents as median values for each gasoline blending components.

- Benzene

There are reported benzene contents in the LIMS for each gasoline blending components.

- Oxygen, oxygenates and ethanol

The database reports oxygen content in the mass percent and oxygenates and ethanol in the volume percent that are from the LIMS as median values.

- DVPE

DVPE is reported in the database in the units of kPa and it is from the LIMS analyses as median value.

- RON and MON

RON and MON are from the LIMS analyses, except for butane, n-and isopentane and ethanol they are from the literature applying the octane numbers of pure compounds (Christensen et al., 2011; Ghosh et al., 2006).

- Sensitivity

Equation 7 shows how the sensitivity is calculated for each gasoline blending components.

$$Sensitivity = RON - MON \quad (7)$$

- AKI

According to Equation 8 is calculated AKI for each gasoline blending components.

$$AKI = \frac{RON+MON}{2} \quad (8)$$

- Sulphur

Sulphur content is in the unit mg/kg and it is a median value from the LIMS analyses.

- Distillation

There are reported the distillation curves for gasoline blending components in the database according to EN ISO 3405 -standard from the LIMS analyses. The database also reports the distilled fractions at 70 and 100 °C for gasoline blending components according to the LIMS analysis.

- C-H-relation and carbon number

Based on the analyses of the LIMS are listed the carbon numbers and C-H -relation of each gasoline blending component in the database. The carbon numbers of more complicate components such as reformate and Cat gas, refer to their typical composition.

- LHV

There are presented the LHVs in the unit MJ/kg and MJ/l in the database that are calculated applying PONAs from the LIMS to investigate the composition of gasoline components. In addition, the Automotive Fuel Reference Book provides the LHVs for individual hydrocarbon compounds. In the LHV calculations are considered hydrocarbons that are over 0.5 wt% present in gasoline blending components. The database reports the average value of the LHV to present the LHV of gasoline component. N-pentane, ETBE, MTBE, TAME and ethanol have heating values from literature applying the LHVs of pure compounds (EFOA, 2006; Owen and Coley, 1995; Christensen et al., 2011).

5.3 The evaluated upgrading units to produce renewable gasoline

In the thesis, four upgrading units, reforming, isomerization, hydrotreating and FCC are researched considering their raw materials. The other units in the refinery like MTBE and alkylation receive their feeds from these units and therefore, they are not included in this evaluation. Thesis researches the operation principles of the units and according that it forms the proposals for the future renewable feedstocks. The reactions, reaction rates and composition of feeds of each upgrading unit are defined to ensure the possible upgrading of renewable feedstocks in them.

6 Results and analysis

The results and analysis chapter presents hydrocarbon compounds that are present in gasoline blending components, the collected database; analysed blending components

and their properties with figures, and the ideal renewable feedstocks into chosen gasoline upgrading units. In the end, the chapter provides the octane blending behaviour of hydrocarbons and oxygenates.

6.1 Explanations for the RON of hydrocarbons in gasoline blending components

Hydrocarbons have different RONs, depending on their structure such as straight chain or cyclic, aromatic ring or double bonds. The results of PONA from LIMS analyses show hydrocarbons that are present in gasoline blending components over 0.5 wt%. This section presents those hydrocarbons and their RONs from literature sources (Owen and Coley, 1995; Ghosh et al., 2006; Schobert, 2013).

Paraffins

In Figure 20 are presented the results of n-paraffins that are present over 0.5 wt% in gasoline blending components and their RONs a function of their carbon number.

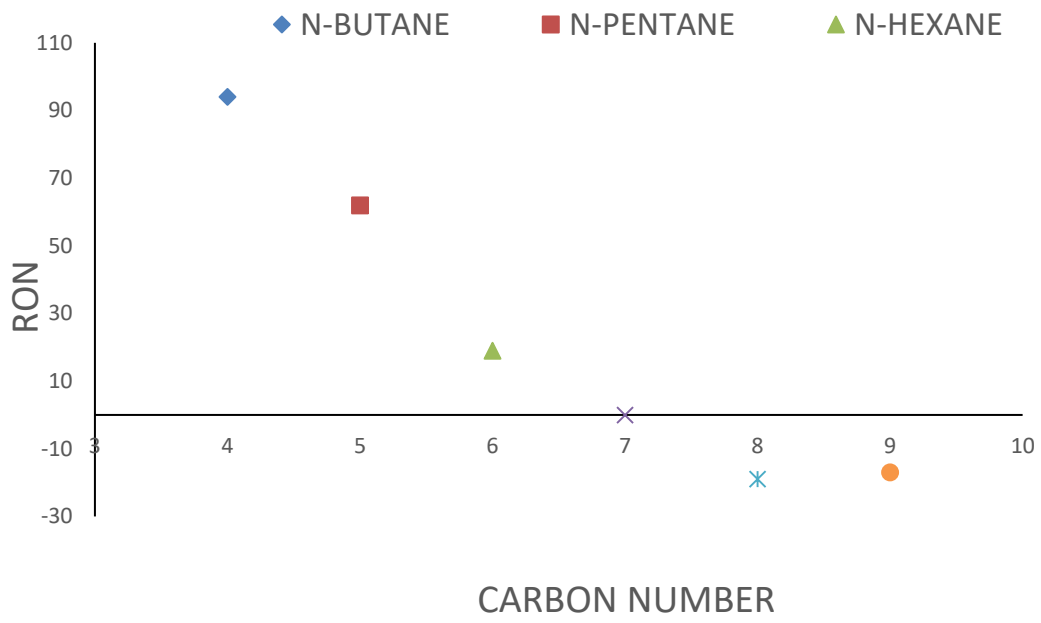

Figure 20. The relations of structure of n-paraffins to their RON (Ghosh et al., 2006; Owen and Coley, 1995).

Figure 20 shows clearly that the longer chain length of n-paraffins decreases their RON, because the amount of reactive secondary C-H bonds increases. For instance, in Figure 20, n-butane has approximately RON 90 otherwise n-pentane has around 60. The RON of n-octane and n-nonane are even negative. In addition to the n-paraffins, gasoline contains also isoparaffins that are listed in Table 4. Moreover, Table 4 shows

the carbon number, RONs and number of methyl groups of isoparaffins that are present in gasoline blending components over 0.5 wt%.

Table 4. Isoparaffins of gasoline blending components (Owen and Coley, 1995; Schobert, 2013).

Isoparaffins	C-number	RON	Methyl groups
2-methylbutane	5	99	1
2,3-dimethylbutane	6	92	2
2-methylpentane	6	73	1
3-methylpentane	6	86	1
2,2-dimethylbutane	6	92	2
2,3-dimethylpentane	7	87	2
2-methylhexane	7	44	1
2,3-dimethylpentane	7	87	2
3-methylhexane	7	56	1
2,4-dimethylpentane	7	77	2
3-Methylheptane	8	30	1
iso-octane	8	100	3
2,5-dimethylhexane	8	-	2
2,4-dimethylhexane	8	65	2
2,2,3-trimethylpentane	8	105	3
2,3,4-trimethylpentane	8	97	3
2,3,3-trimethylpentane	8	100	3
2-methylheptane	8	13	1
2,3-dimethylhexane	8	71	2
4-methylheptane	8	31	1
4-methyloctane	9	-	1
3-methyloctane	9	-	1
2-methyloctane	9	-	1
2,2,5-trimethylhexane	9	91	3

What stands out in Table 4 is the wide amount of isoparaffins in gasoline blending components and they differ among their C-number and number of methyl groups. Figure 21 presents the RON a function of C-number of isoparaffins when the number of methyl groups differs.

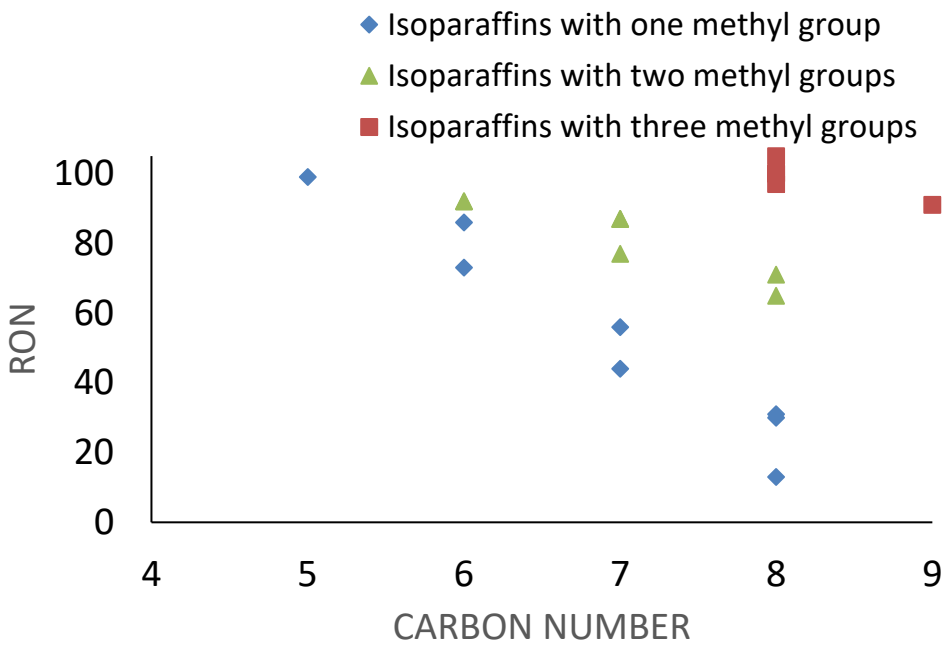

Figure 21. More branched isoparaffins have higher RON (Owen and Coley, 1995; Schobert, 2013).

What is clear in Figure 21 is the declining trend of RON when the carbon number of isoparaffins increases. There are still exceptions in this trend, because the amount of methyl groups influences on the RON significantly. Green triangles are always top of the blue squares when the carbon number stays same in Figure 21 which proves that the RON increases when hydrocarbon is more branched. For instance, C8 isoparaffins could have one methyl group, two or three and Figure 21 shows that the highest RON belongs to compounds with the three methyl groups. Explanation for that is the increase of the primary C-H bonds in their carbon backbone. Those bonds are less reactive than secondary ones that isoparaffins with one or two methyl groups have. De Bruycker et al. explained the difference between RONs of isoparaffins with BDE. The primary C-H bonds has higher BDE that decreases their reactivity and increases their RONs (De Bruycker et al., 2016).

In addition to the amount of methyl groups, their position in the carbon backbone affects to the RON that Table 4 illustrates with blue colour between 2-methylpentane and 3-methylpentane and with green colour between 2-methylheptane and 4-methylheptane. If the methyl group is in the more centre of the carbon backbone, it increases the RON. The reason for that is the shorter paraffin chain length that reduces the reactivity of compound. Therefore, the reactivity of 3-methylpentane and 4-methylheptane decreases and their RONs increase.

Figures 20 and 21 show the same trend when carbon number increases, but the RONs of isoparaffins are always higher with the same carbon number than those of n-paraffins. Schobert noticed this trend and explained it with the smaller surface area of isoparaffins (Schobert, 2013). Higher surface area of n-paraffins forms more reactive

radicals during the bimolecular initiation reactions that interact via London-forces with oxygen. While the branching causes smaller surface area to isoparaffins that prevents the formation of reactive radicals that decreases the probability of their autoignition.

Aromatics

Table 5 shows the results of aromatics that are present over 0.5 wt% in gasoline blending components. It also presents the C-number, RON and amount of methyl, ethyl and propyl groups in compounds.

Table 5. The PONA results of aromatics in gasoline blending components (Owen and Coley, 1995; Schobert, 2013).

Aromatics	C-number	RON	Methyl groups	Ethyl groups	Propyl groups
BENZENE	6	99	0		
TOLUENE	7	124	1		
ETHYLBENZENE	8	124	0	1	
META-XYLENE	8	145	2		
PARA-XYLENE	8	146	2		
ORTO-XYLENE	8	120	2		
ISOPROPYLBENZENE	9	132	0		1
N-PROPYLBENZENE	9	127	0		1
META-ETHYLTOLUENE	9	162	1	1	
PARA-ETHYLTOLUENE	9	155	1	1	
1,3,5-TRIMETHYLBENZENE	9	171	3		
ORTO-ETHYLTOLUENE	9	125	1	1	
1,2,4-TRIMETHYLBENZENE	9	148	3		
1,2,3-TRIMETHYLBENZENE	9	118	3		
1-METHYL-3-PROPYLBENZENE	10		1		1
C4-BENZENE	10	114			
1,2,4,5-TETRAMETHYLBENZENE	10		4		
1,2,3,5-TETRAMETHYLBENZENE	10	154	4		

Table 5 shows that RONs are high and their variation between different aromatics are significant. For instance, ortho-ethyltoluene and meta-ethyltoluene have the RONs 125 and 162 as Table 5 indicates with the blue colour even though the only difference between them is the position of methyl groups. Figure 22 shows the RON a function of carbon number when number of methyl groups increases in aromatics.

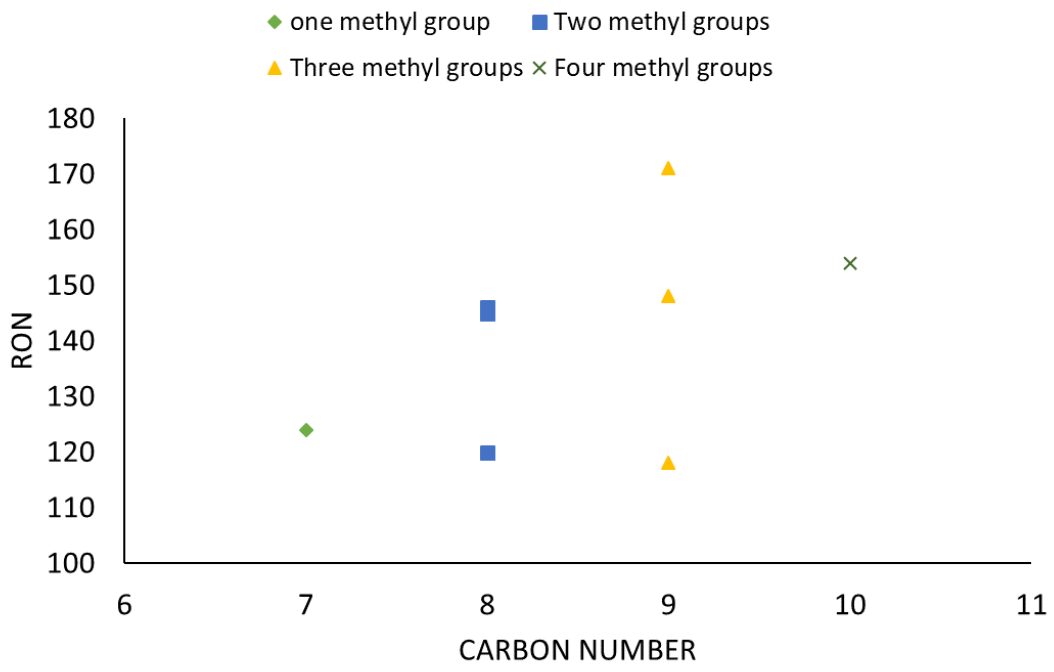

Figure 22. The side groups increase the RON of aromatics (Owen and Coley, 1995; Schobert, 2013).

What stands out from Figure 22 is the linear increase of RON from aromate with one methyl group to aromate with three methyl groups. The highest and lowest RONs belong to aromatics with three methyl groups. Table 5 shows with green colour that 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene have RONs of 171 and 148, while 1,2,3-trimethylbenzene has only 118. The positions of methyl groups in aromatic ring could explain the low RON value, 118. 1,2,3-trimethylbenzene has methyl groups in the adjacent carbons, while the methyl groups of other two aromatic compounds are further each other. Boot et al. researched the effect of the methyl groups on the RON of aromatics and noticed that they boost it, because they form resonance stable radicals during bond scission (Boot et al., 2017). Those stable radicals are not reactive that reduces their autoignition reactions with oxygen. There is not a lot research available about the position of the methyl, ethyl and propyl groups in aromatic ring that would be interesting to research more to find out its influence on the RON of gasoline. Already Figure 22 proves that the positions need to be considered to evaluate the RON of aromatics.

The longer side group such as ethyl or propyl groups decreases the RON compared to the same carbon number aromatics that Table 5 shows with red colour. Those longer groups increase the number of the secondary C-H -bonds that increase the reactivity of compound. There are still exceptions in this trend such as aromatic that has methyl group and in addition to that ethyl group that the Table 5 shows with yellow colour. Figure 23 presents the RON in a function of carbon number when the length of the side group increases.

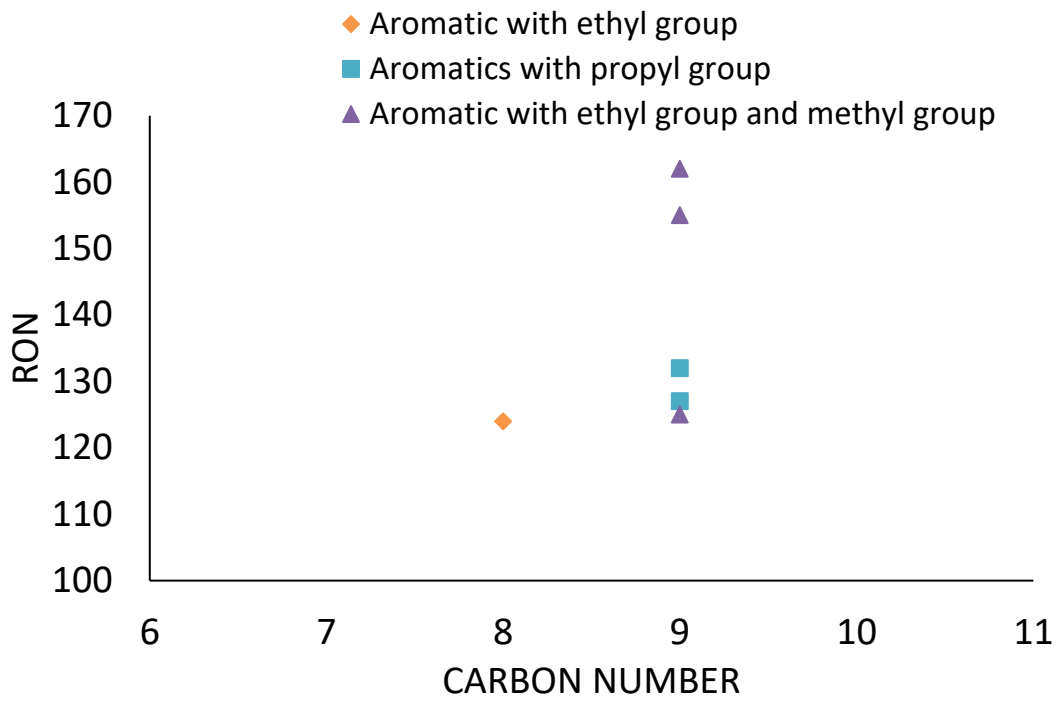

Figure 23. The longer side groups decrease the RON compared to methyl groups (Owen and Coley, 1995; Schobert, 2013).

In Figure 23, the highest RONs belongs to aromatics with ethyl and methyl group, because the methyl group increases the amount of primary C-H -bonds that increases its RON. There can be seen the same trend in Figure 23 that the thesis noticed before in the case of 1,2,3-trimethylbenzene in Figure 22. One aromatic with ethyl group and methyl group has the lowest RON of C9 aromatics that is explained by the position of the side groups. Table 5 indicates with blue colour compound to be ortho-ethyltoluene that has methyl and ethyl groups in the adjacent carbons and therefore, it has lower RON compared to para-ethyltoluene or meta-ethyltoluene.

Naphthenes

Naphthenes are cyclic hydrocarbons, with or without double bonds, that are favoured feedstock compounds into the gasoline upgrading units. They have high RONs that Table 6 presents, but they are more reactive than aromatics, because the absence of delocalized electrons. In Table 6 are presented the results of naphthenes that exist in gasoline components over 0.5 wt%.

Table 6. Naphthenes of gasoline blending components (Schobert, 2013).

Naphthenes	C-number	RON
cyclopentane	5	101
cyclohexane	6	83
methylcyclopentane	6	91
cis-1,3-dimethylcyclopentane	7	-
trans-1,3-dimethylcyclopentane	7	-
methylcyclohexane	7	75
ethylcyclopentane	7	-
cis-1,3-dimethylcyclohexane	8	67
C3-cyclohexane	9	-

What stands out from Table 6 is the highest RON of simple cycloalkanes, cyclopentane with the blue colour, otherwise methylcyclopentane with the green colour has distinctly lower RON. Table 6 indicates the same in the case of cyclohexane with the yellow colour and methylcyclohexane with the grey colour, even though the difference is not as high in that case. The difference between RONs of cyclopentane and methylcyclopentane depends on the amount of secondary C-H -bonds. Methylcyclopentane has four secondary carbons and one tertiary carbon that increases its reactivity. While cyclopentane has five secondary carbons but does not contain any tertiary ones. What is also relevant this Table 6 is the slight difference between RONs of cyclohexane and methylcyclopentane. The eight secondary C-H bonds in methylcyclopentane explains its lower reactivity compared to cyclohexane that has 12 of those bonds.
There is also naphthene that has two methyl groups with the red colour in Table 6, cis-1,3-dimethylcyclohexane and it has the lowest RON among naphthenes. The explanation for that is the highest number of tertiary C-H bonds that increases its reactivity.

Olefins

Olefins are the fourth hydrocarbon group in gasoline that have an influence on the RON. Table 7 shows the results of olefins that are present over 0.5 wt% in gasoline blending components and lists their RONs, carbon numbers and indicates the carbon that has the methyl group.

Table 7. The RONs of olefins that exist in gasoline over 0.5 wt% (Owen and Coley, 1995).

Olefins	C-number	RON	Place of the methyl group in the carbon backbone
3-methyl-1-butene	5	129	3
2-methyl-1-butene	5	146	2
trans-2-pentene	5	150	
Cis-2-pentene	5	154	
2-methyl-2-butene	5	176	2
trans-4-methyl-2-pentene	6	130	4
2-methyl-1-pentene	6	126	2
Cis-3-hexene	6		
trans-3-hexene	6	137	
trans-2-hexene	6	134	
2-methyl-2-pentene	6	159	2
cis-2-hexene	6	-	
trans-3-methyl-2-pentene	6	130	3
C7 olefin	7	-	
2-methyl-2-hexene	7	129	2
C8 olefin	8	-	

Figure 24 indicates the differences of the RONs between olefins that have double bond or methyl group in the different positions of carbon backbone.

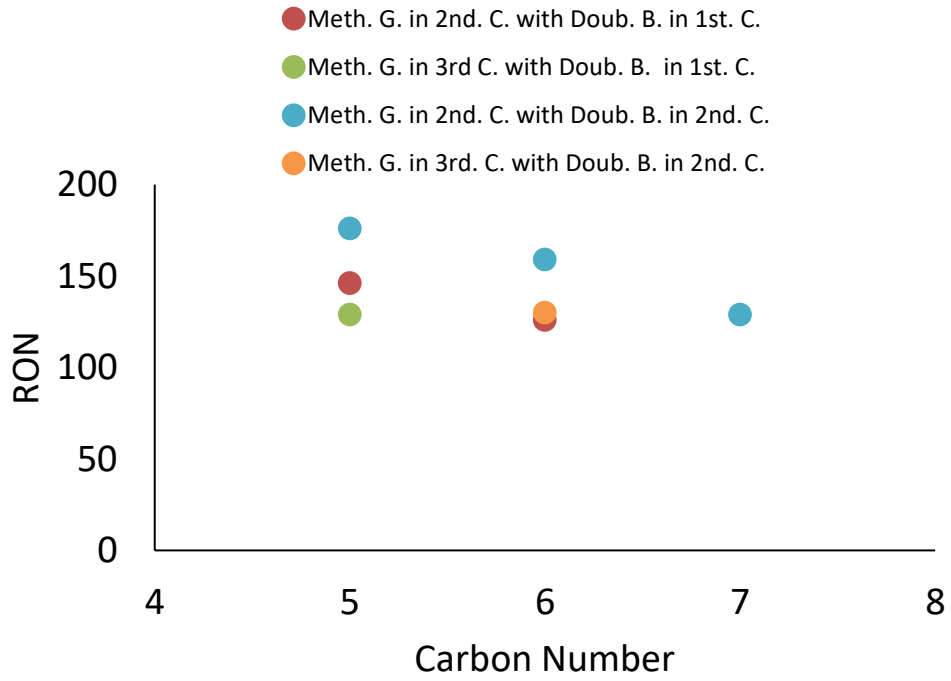

Figure 24. The position of double bond in olefin influence on its reactivity and in addition to that, the position of methyl group affects to their RON, too (Owen and Coley, 1995).

There can be noticed the obvious trend of olefins with methyl group and double bond in the second carbon in Figure 24. It presents the linear decrease of RON when the carbon number increases of these compounds that table 7 present with the blue colour. There can be noticed also difference of RONs in Figure 24 when the position of double bond changes in olefins. For instance, olefins with red colour in Figure 24 have double bond in the first carbon that increases their reactivity and decreases their RON compared to olefins with blue colour in Figure 24 that have the same carbon number, but their double bond is in the second carbon. Bounaceur et al. noticed this same trend and explained the effect of position of double bond to the RON by BDE (Bounaceur et al., 2009). The BDE of tertiary C-H bonds is the lowest and the bond breaks easy, while secondary and primary C-H bonds have higher BDEs. Table 7 shows the RON of trans-3-hexene with the yellow colour to be 137 otherwise trans-2-hexene with the orange colour has RON 134. They both have four secondary C-H -bonds, but trans-3-hexene has a shorter paraffinic carbon backbone that explains its lower reactivity. In Table 7 is shown also the difference of RONs between 2-methyl-2-butene with the blue colour and 2-methyl-1-butene with the green colour, 176 and 146. The latter has significantly lower RON, because it has only six primary C-H bonds compared to nine of 2-methyl-2-butene.

What is also interesting in Figure 24 is the difference of RONs between three compounds with the carbon number five. These compounds have different amount of the primary bonds that influence on their reactivity. There are compounds with green and red colour in Figure 24 that have lower RON than compound with blue colour, because they contain only six primary C-H -bonds. While compound with blue colour has nine C-H -bonds. What needs to be still explained is the difference of RON between the red and green compounds in Figure 24. It depends on the amount of the tertiary bonds that green compound has more and therefore, its RON is also lower.

The above-mentioned hydrocarbons are results of the PONA analysis of gasoline blending components and the RONs are literature values. The reliability of the analysis is high, because the PONA analysis is an accurate method to analyze the composition of gasoline blending components. However, the time interval of the analysis is 15 years as longest and therefore, the changes in the compositions of components are possible. Nevertheless, the operating principles of the upgrading units are continuously similar that does not cause significant variations for the composition of blending components.

Three different sources provide the RON values that also increases inaccuracy, because the methods to calculate them might differ. However, their order of magnitude is more important than the exact values, because the target of the thesis is to present differences between RONs of hydrocarbon groups to prove their influence on RON of gasoline.

6.2 The properties of gasoline blending components

The property database for gasoline blending components is built on based on the properties that are used in the blending design and, also properties, which are expected to be useful in the future. Moreover, the FQD has limits for most of those values that gasoline production needs to follow. Table 8 presents those properties and Table 9 lists gasoline blending components.

Table 8. The properties of gasoline blending components to optimize blending.

Properties			
Density	RON and MON	Sulphur	LHV
Hydrocarbon contents: n-and isoparaffins, olefins, aromatics, naphthenes, benzene	Oxygen, oxygenates and ethanol	Distillation curve and evaporated volumes at 70 and 100 °C	Sensitivity
AKI	DVPE	C/H relation and Carbon number	The amount of analysis per component

Table 9. Gasoline blending components.

Gasoline blending components	
Isopentane	TAME
n-pentane	Ethanol
Butane	Cat gas
Alkylate	Reformate
Isomerate	ETBE
Light gasoline component	MTBE

Aromatics and paraffins are the main hydrocarbon groups in gasoline blending components and olefins and naphthenes are the minority groups according to the database. Olefins are hydrogenated from light gasoline fractions before more upgrading and therefore, their share is low. In the database are classified paraffins into n-and isoparaffins that provides more accurate explanations to the octane numbers of blending components.

What is important to notice from the database is the oxygenate content of blending components that is almost zero, while for ether blending components and ethanol it is high. Ethanol is usually denatured by ethers for instance, and therefore, it is not pure.

Oxygenates are important blending components for gasoline production due to their high RON, but oxygen in their structure decreases the energy density of gasoline.
The hydrocarbon structure is the key property for the gasoline production, because it forecasts other properties of gasoline such as RON and DVPE. Heavier blending components have lower DVPE than lighter ones that needs to consider in the gasoline blending during the different seasons. Figure 25 shows how much the density could vary between different gasoline blending components.

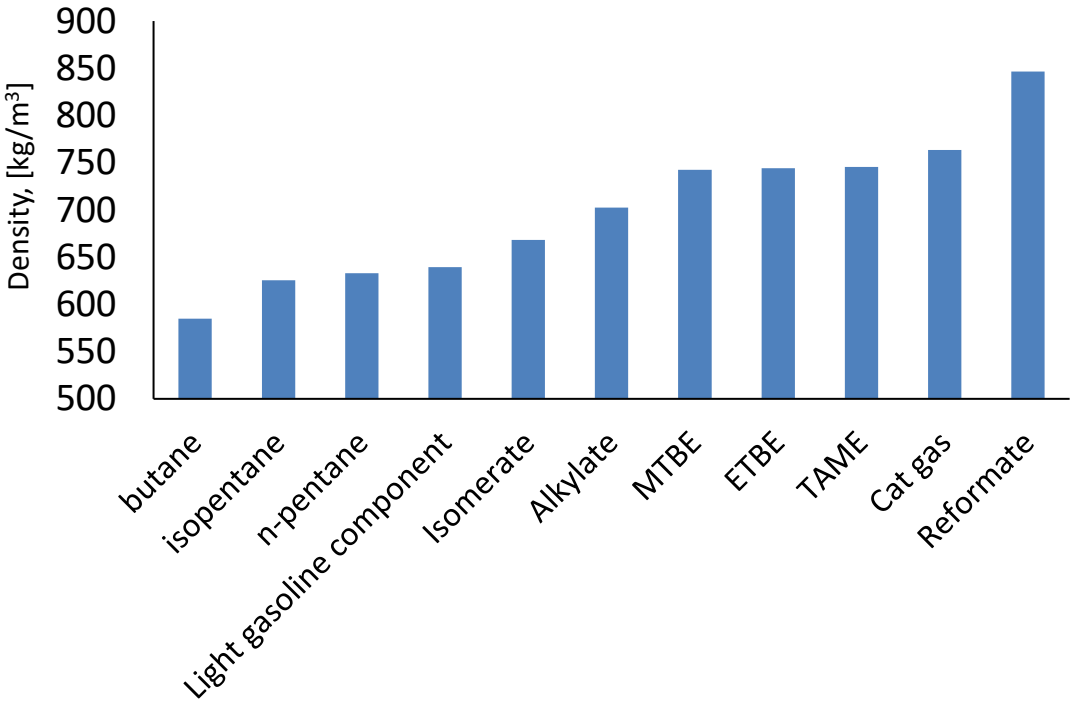

Figure 25. There are variations among densities in the gasoline blending components (LIMS, Neste).

There are variations in the DVPE between light and heavy components, for instance butane is the lightest component like Figure 25 shows, and it has the highest DVPE. While reformate is the heaviest component that indicates its low DVPE. Moreover, the EN 228 limits the density of gasoline, from 720 to 775 kg/m^3 and assets limitations for blending of the heaviest components together.
The most aromatic components have the highest RONs of non-oxygenate blending components compared to mainly n-paraffinic components. MTBE, ETBE and ethanol have been noticed to have even higher RONs. The MONs of blending components are lower than RONs for almost every component, except n-paraffinic components. Longer chain length of n-paraffins increases the MON and decreases the RON. Their difference is called sensitivity, and the database reports that value. Higher sensitivity

is considered valuable property in the downsized boosted SI-engines in the future, because it could improve the ignition properties of gasoline. Figure 26 presents the variations of sensitivity of gasoline blending components.

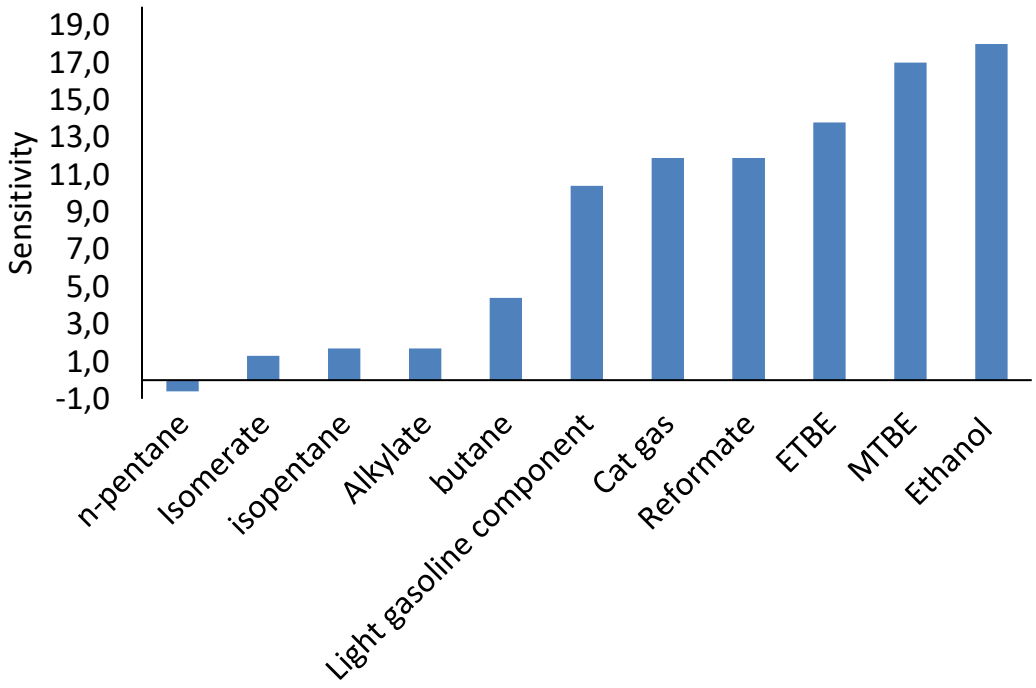

Figure 26. The sensitivity describes the difference between RON and MON (LIMS, Neste).

In Figure 26 is shown that oxygenates have the highest sensitivity otherwise n-and isoparaffinic components have the lowest. N-paraffinic components have even slightly negative referring to higher MON than RON. Generally, can be concluded that aromatic and oxygenate components have high sensitivity that rises their interest as gasoline blending components, while the sensitivity of paraffins is almost zero or even negative in the case of long n-paraffins.

In addition to sensitivity, LHV is an important value to evaluate the possible future feedstocks for gasoline production, because it describes how much energy gasoline releases during combustion. Therefore, high LHV is favoured to minimize the fuel consumption and emissions. Also, in the case of higher ethanol contents of gasoline blends the heating value need to be consider, because LHV of ethanol is significantly lower than gasoline. Figure 27 shows the heating values of gasoline blending components in the units of megajoules per litre.

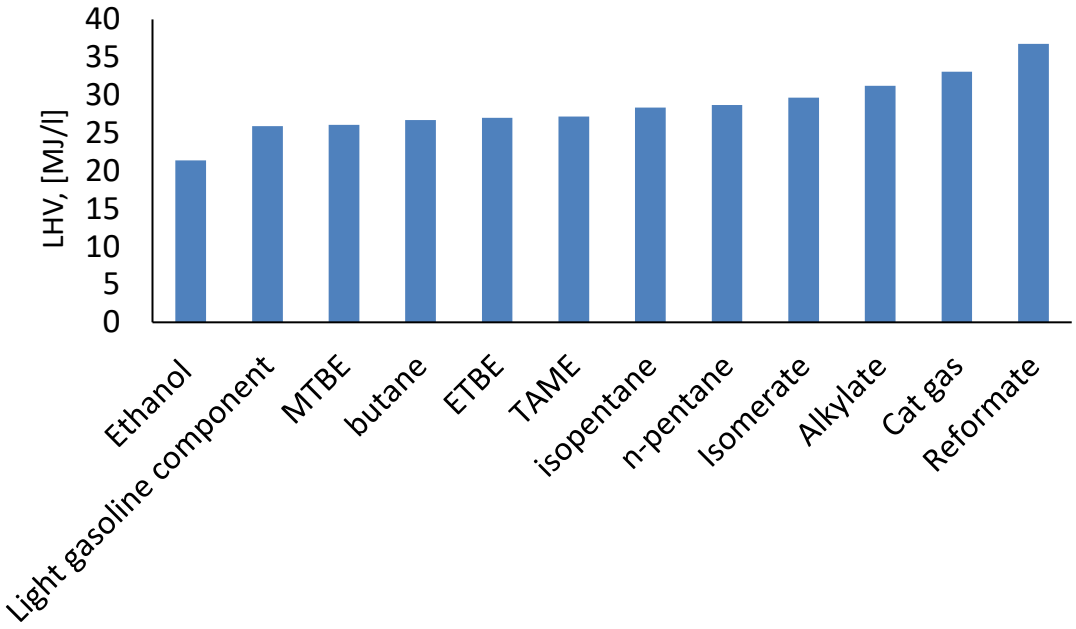

Figure 27. The high LHV is desired property in gasoline (LIMS, Neste).

Usually, the heat release from gasoline is wanted to know per litre, because gasoline is also purchased by the customers in the same unit in the fuel stations. Heaviest gasoline components have the highest volumetric LHVs, otherwise ethanol has the lowest, because of oxygen in its structure that contains no energy. Moreover, the carbon chain of ethanol is short that causes the high oxygen-to-carbon ratio. Paraffins and light gasoline component have also low volumetric LHVs and the latter even lower than ethers. Figure 28 shows the mass based LHVs of gasoline components.

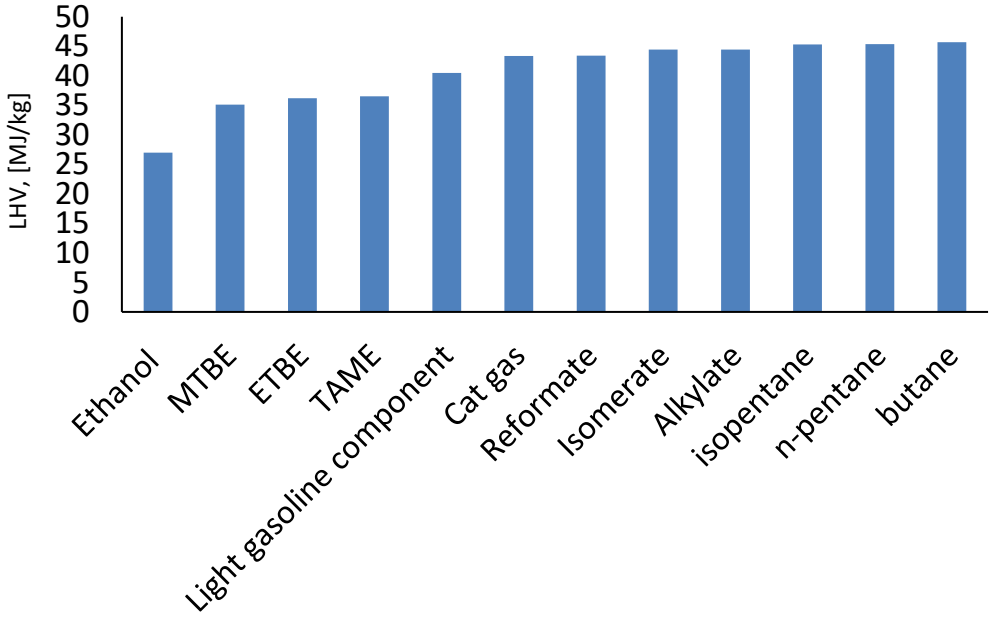

Figure 28. The LHV in the units of MJ/kg (LIMS, Neste).

What is obvious in Figures 27 and 28 is that the density of components explains the differences between the released heat during combustion; higher density components release more energy with equal volume than lighter ones and therefore, heavier components can be applied less to fill the needed energy output.

An interesting property to consider for gasoline is the C/H-relation, because it has an influence on gasoline consumption due to higher energy content of hydrogen compared to carbon. This thesis found earlier that the 2% decrease of carbon content will decrease the CO_2 emissions 5%. Therefore, gasoline components with lower C/H-relation bring more energy into gasoline.

The comparison of C/H-relations of blending components shows that oxygenates has lower compared to hydrocarbons. Moreover, paraffins have low relations, because their short carbon backbones and single bonds. These results promote the use of these components in gasoline blending to decrease fuel consumption and CO_2 emissions.

In the database are reported also the distillation curves of each blending component, except butane which distillation data was not available. Figure 29 presents the distillation curves for the blending components.

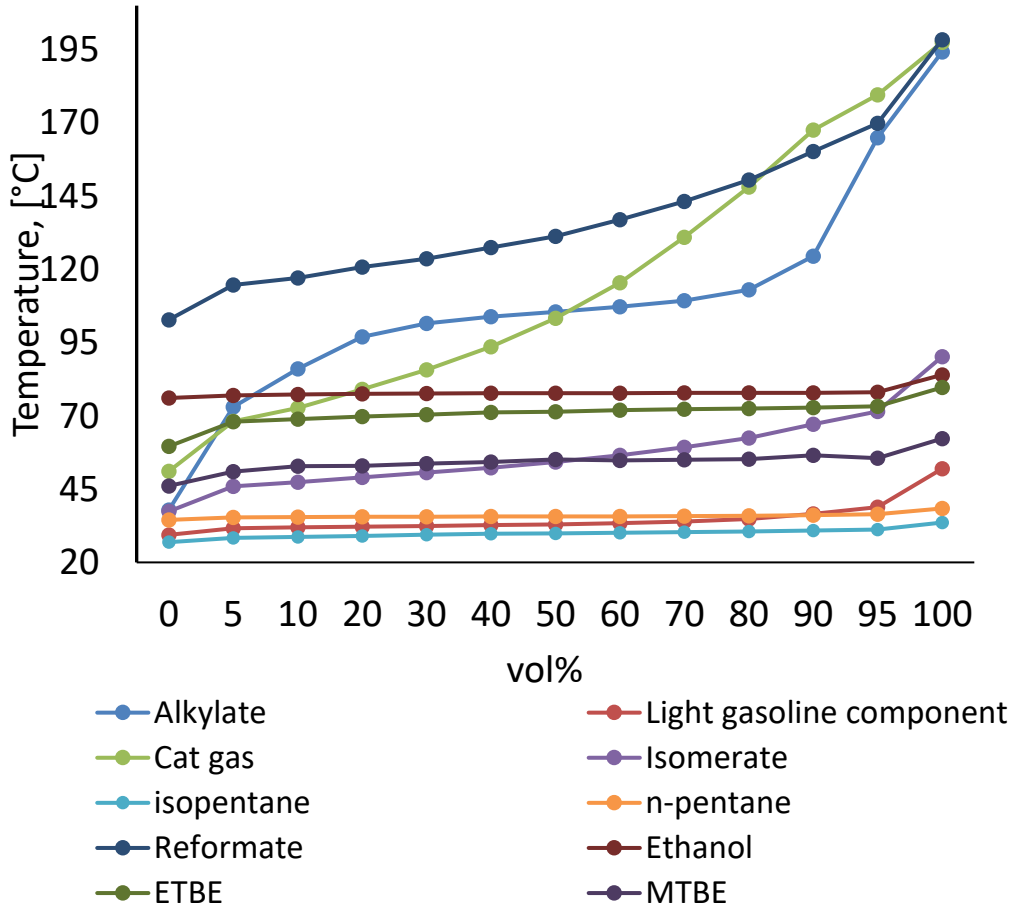

Figure 29. The distillation end point of gasoline is 210 °C according the FQD which all gasoline components need to also fulfill (LIMS, Neste).

Figure 29 shows that lighter blending components, isomerate, light gasoline component, paraffins and oxygenates have the lowest boiling points. While the highest boiling points belong to alkylate, Cat gas and reformate. Compared the distillation curves in Figure 29 to the DVPEs of blending components is noticed their relation. Gasoline components that have high DVPE have also their final point of distillation at lower temperatures. While gasoline components that have low DVPE reach their final point of distillation at higher temperatures. Almost pure blending components, n-and isopentane, distillates within 10 °C and that same distillation behaviour has ethanol as noticed from Figure 29.

There are also sulphur contents of gasoline blending components in the database, because the FQD limits it to 10 mg/kg. Sulphur is known as the catalyst poison and therefore, the feed into the upgrading units such as into reforming and FCC, is hydrotreated before them. The hydro-desulphurization units remove sulphur from blending components.

6.3 The possible future feeds to the gasoline upgrading units

This section presents the ideal feed for the FCC, isomerization, reforming and hydrotreating units and proposes the possible renewable feed them in the future. In the literature part of this thesis is researched the renewable feedstocks, and this section presents their upgrading methods in the four units. Table 10 concludes the feed, reactions, reaction rates and the hydrocarbon structure of produced gasoline blending components from these four units.

Table 10. The presentation of the four gasoline upgrading units according their feed, reactions, reaction rates and the hydrocarbon structure of produced gasoline blending components.

unit	feed	reactions	reaction rates	main products
FCC	C20-C25 paraffins, long olefins, cyclo naphthenes (C10)	cracking, isomerization, hydrogen transfer	-	olefins (C5-C8), isoparaffins (C5-C9), aromatics (C6-C10), p-naphthenes (C6-C9), o-naphthenes (C6-C9)
Hydrotreating	C5-C12 paraffins, alkenes and cycloalkenes	hydrogenation of alkenes and cycloalkenes	hydrogenation >hydrocracking	C7-C11 naphthenes, hexane, n-and isopentane and C3/C4-fractions
Reforming	heavy naphtha range hydrocarbons: C6-C11 naphthenes and paraffins	aromatization, isomerization, cyclization, dealkylation, hydrocracking	aromatization>isomerization>cyclization	3/4 aromatics (C7-C9) and 1/4 isoparaffins (C7-C8)
Isomerization	n-pentane and n-hexane	isomerization	isomerization>hydrogenation and decyclization	isopentane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane

In Table 10, the feed column is the most important for estimation the renewable feedstocks for the future. Moreover, the reactions that occur in the units and their reaction rates are valuable information for that. What is clear in Table 10 is the variation of feed properties that provides the possibility to use versatile hydrocarbon sources. However, it is also challenging, because the same feed cannot utilize for all units. Table 10 shows that hydrotreating unit handles C5-C12 paraffins, alkenes and cycloalkenes that are suitable after treating to the reforming and the isomerization units. Therefore, one renewable feedstock for the hydrotreating unit could increase production of renewable gasoline also in other units.

Hydrotreating

There are several hydrotreating units in the refineries and they pre-treat the feeds into next upgrading units by removing sulphur with hydrogen. Simultaneously, it hydrogenates alkenes and cycloalkenes to paraffins and naphthenes. The unit produces pentanes and hexanes for the isomerization, heavy gasoline component for the reforming and liquefied gases.
In the ideal feed into hydrotreating unit consists of low aromatic, C5-C12 short carbon chain paraffins, alkenes or cycloalkenes that it hydrogenates. At higher temperature, hydrocracking could also occur. The products of the unit consist of straight chain and cyclic C7-C11 hydrocarbons, n-and iso-pentanes and liquefied gas fractions. Table 11 summarizes the feed with red colour, reactions and with the yellow colour products in the hydrotreating unit.

Table 11. The feed, reactions and products of the hydrotreating unit.

Reactions	C7-C11 to reforming	Hexane to isomerization	n- and iso-pentane	C3/C4-fractions
Hydrogenation of alkenes and cycloalkenes	C5-C12	C5-C12	C5	The fraction is removed by butane removal
Hydrocracking	C5-C12	C5-C12	C5-C12	-

What is noticed in Table 11 are the two reaction pathways for producing different hydrocarbon structures. From these two, the hydrogenation of alkenes and cycloalkenes is the main reaction pathway in the unit besides sulphur removal reactions. Hydrocracking reactions are not prominent and desired, because they decrease the activity of catalyst and partial pressure of hydrogen. However, during hydrogenation of high olefinic compounds, is extremely important to control the outlet temperature of hydrotreating reactor and the need of preheating of feed to avoid too high temperatures. It could be also possible to hydrotreat oxygen containing components in these units

such as ketones and furans with the catalyst modification in the future and thus, widen the raw material options. Because the hydrotreating is a pre-treatment unit of the three other units, its alternative feeds are presented in the next sections.

Fluidized catalytic Cracking

Cat gas consists mainly the three hydrocarbon groups: olefins, aromatics and isoparaffins that shares vary in the gasoline component depending on the refineries. The versatile composition of Cat gas proves the complexity of FCC unit and, also it is a challenge to find ideal feed for it. The various hydrocarbon groups in Cat gas improve its blending with other blending components but can also be a disadvantage due to different chemistry of the hydrocarbon groups.
There are long chain hydrocarbons in ideal feed for the FCC unit that cracking, isomerization and hydrogen transfer upgrade to iso-olefin, aromatic and iso-paraffinic rich blending component. Optimal hydrocarbons for these reactions are paraffins and olefins. Aromatics and especially, polyaromatics, are problematic feedstocks because they form coke that decreases the activity of catalyst and increases its regeneration need. Table 12 concludes the ideal feed with red colour, reactions and with yellow colour desired hydrocarbons in the FCC unit.

Table 12. The ideal reactions in the FCC unit and the ideal feed for these reactions to produce Cat gas gasoline blending component.

Reactions	olefins	aromatics	isoparaffins
Cracking	Long olefins	Aromatics with long alkyl chain (ArC10H2)	Aromatics with long alkyl chain (ArC10H2), long paraffins, cyclic naphthenes
Isomerization	Olefin bond shift in olefin structure, n-olefins	-	n-paraffins
Hydrogen transfer	-	Long olefins, Long olefin + naphthene	Long olefins, Long olefin + naphthene

Table 12 shows the different reaction pathways to produce many hydrocarbon structures only changing the feedstock such as cracking produces olefins, isoparaffins and aromatics. However, all reactions cannot produce aromatics and olefins and therefore, the reaction conditions or feedstock need to define the way that the production is optimized.
The possible renewable feedstocks for the cracking reactions are squalene and α-limonene. α -limonene is cracked into aromatics and paraffins, while squalene is cracked into shorter olefins. Other option is to first hydrogenate squalene to remove double

bonds in the hydrotreating unit from heavy gas oil fractions. The hydrotreating of squalene could produce long isoparaffins that are possible feed into FCC unit where they are cracked shorter chains.
Other reaction type in the FCC unit is hydrogen transfer that produces aromatics and paraffins as well. α -limonene and α -pinene are possible for this reaction with the pretreatment. The first step is their hydrogenation to produce C10 naphthenes that then react in the FCC unit with squalene via hydrogen transfer reaction to produce aromatics and paraffins. However, those paraffins from hydrogen transfer reactions might be too long for Cat gas component that requires their cracking to C5-C9 paraffins.

Reforming

There are roughly 85% of aromatics and 15% of isoparaffins in the hydrocarbon composition of reformate. The carbon number of aromatics is from C7 to C9 and of isoparaffins C7. Those hydrocarbons together increase the RON of reformate and increase its value as gasoline blending component.
The ideal feedstocks into the reforming unit are from C7 to C11 n- and isoparaffins and naphthenes. In the hydrotreating unit, the double bonds of feedstocks are hydrogenated that produces heavy gasoline component. This gasoline components are applied straight as a blending component or dehydrogenated in the reforming unit to increase its RON. Table 13 presents the ideal reactions in the reforming unit, its optimal hydrocarbon structure of feed with red colour and desired products with yellow colour.

Table 13. The reactions and the reactants to produce the reformate blending component.

Reactions	Aromatics	Paraffins
dehydrogenation/aromatization	naphthenes with side chains	-
isomerization	-	n-paraffins
dehydrocyclization	paraffins	-
dealkylation	Aromatic compounds with alkyl side chains	

From Table 13 can be concluded that the aromatization, isomerization, dehydrocyclization and dealkylation are the main reactions in the reforming unit. The reforming unit dehydrogenates naphthenes into aromatics and isomerizes n-paraffins to isoparaffins or dehydrocyclizes them to aromatics. Aromatics can also be feedstocks, if they have long side chains or multiple side chains. Those aromatics are dealkylated into aromatic ring and paraffins. The aromatization occurs most likely in the reforming reaction conditions, while cyclization and isomerization are next reactions before hydrocracking. Table 14 shows the reactions rates of the reforming reactions.

Table 14. The reaction rates in the reforming unit.

Reaction	Reaction rate
Aromatization	100
Isomerization	10
Cyclization and hydrocracking	1

What stands out in Table 14 is the ten times higher probability of the aromatization than the isomerization and even 100 times higher than the hydrocracking in reforming conditions. The advantage of these reaction rates is the high yield of aromatics and less hydrocracked hydrocarbons that are not desired because they increase hydrogen consumption and decrease the activity of catalyst.

There are α -limonene and α -pinene, the possible renewable feeds to produce aromatics in the reforming unit. First the hydrotreating unit hydrogenates α -limonene to cyclohexane with one methyl group and isopropyl group and α -pinene to cyclohexane with four methyl groups. Roberge et al. and Tracy et al. studied the hydrogenation of these monoterpenes and they managed to remove double bonds and obtained naphthenes that are possible to further upgrade into gasoline blending components (Roberge et al., 2001; Tracy et al., 2009).

The hydrotreating of high concentration olefinic compounds is a challenge for the operation of the unit, because the temperature could increase significantly in the reactor. However, with a proper control of preheating and outlet temperature of reactor is produced desired naphthenes that the reforming unit aromatizes to produce C4-aromatics. The further reaction is still possible after aromatization, the dealkylation that removes alkyl side chains from aromatics.

Other method to produce aromatics is dehydrocyclization of paraffins that follows their aromatization. For this reaction the possible renewable feedstock is monoterpene, myrcene that loses its double bonds during hydrogenation and then the reforming unit cyclizes and aromatizes it. However, the reaction rates reveal the isomerization reaction to be more rapid than cyclization. Therefore, myrcene is most likely to be isomerized first in the reforming unit that produces desired isoparaffins. Moreover, the hydrocracking is a possible reaction, but it is undesired due to its high hydrogen consumption. That reaction has the lowest reaction rate and therefore, it is not probable reaction to occur before isomerization of myrcene.

Isomerization

Isomerate blending component is mainly isoparaffinic with low amounts of n-paraffins and naphthenes. Main isoparaffins are isopentane and different isomers of isohexane, while its aromatic and olefin contents are practically zero. In the isomerization unit,

the main reaction is isomerization, while hydrogenation and decyclization are the side reactions. Table 15 presents those reactions and with the red colour hydrocarbon groups that form iso-pentanes and iso-hexanes that yellow colour indicates.

Table 15. The isomerization of n-paraffins produces high octane isoparaffins.

Reactions	Isopentane	Isohexane
Isomerization	n-pentane	n-hexane
Hydrogenation	-	Benzene
Decyclization	Naphthenes	

The hydrogenation of benzene is a possible reaction as Table 15 shows, but it is exothermic and therefore, it increases temperature that causes challenges for temperature controlling during isomerization reactions. While the other side reaction, decyclization of naphthenes, decreases the activity of catalyst and thus, reduces reaction rate of isomerization. Therefore, the best feeds for the isomerization unit are n-pentane and n-hexane to avoid those side reactions.

DMF could be a potential feedstock for renewable gasoline production that isomerization unit upgrades. The feed into isomerization unit comes from the hydrotreating unit that purifies it from sulphur and saturates double bonds. Moreover, DMF contains oxygen that HDO removes releasing simultaneously water unlike the conventional hydrotreating. Sacia et al. studied the HDO of DMF and managed to produce n-hexane applying four hydrogen molecules during reaction (Sacia et al., 2015). The release of water is a problem with the existing catalysts in the hydrotreating, but their modification to treat water could allow the utilization of DMF.

In the isomerization unit n-hexane is isomerized rapidly into 3- or 2-methylpentane, while the reverse reaction back to n-hexane is not likely due to higher reaction rate from n-hexanes to isohexanes. The isomerization reactions proceed further to form 2,3-dimethylbutane, but the lower reaction rate retards their formation. Therefore, the production of 3-and 2-methylpentane is more probable in the isomerization conditions.

In addition to DMF, 2,5-dimethyltetrahydrofuran could be a possible feedstock into isomerization unit. Its chemical structure is similar than DMF except the absence of double bonds that decreases the hydrogen consumption during the hydrotreating. The isomerization of 2,5-dimethyltetrahydrofuran follows the same reaction rates than DMF has.

In addition to furans, ketones are possible renewable feedstocks into isomerization unit, especially MIBK, is an option. It is six-carbon ketone and a renewable feedstock. As furans, also MIBK runs through the hydrotreating unit that removes oxygen and produces 2-methylpentane. This compound is an ideal feedstock for the isomerization, because its further isomerization reactions produce more branched isoparaffins, 2,3-

dimethylbutane, if the temperature stays low. Moreover, its de-isomerization to n-hexane is improbable.

This section proposed the renewable feedstocks in the existing gasoline upgrading units attempting to produce renewable gasoline in the future. The problems of the feedstocks concern their too long carbon chain, several double bonds and the presence of oxygen in them. The development of catalysts and optimizing the right process conditions like temperature could solve these problems. However, these feedstock proposals need still more investigation about their availability and viability in the gasoline production.

6.4 Blend proposals

In the results of database is proved gasoline blending components to consist over ten blending components that have hundreds of different hydrocarbons. The octane blending of these components together can be linear or non-linear. This section shows, which hydrocarbon groups and other organic compounds blend together linearly and which synergistic or antagonistic. Table 16 concludes the octane blending behaviour of hydrocarbons and other organic compounds. It indicates with green colour the linearity, with the red and yellow antagonism and synergism and with the blue colour is indicated the need for more research.

Table 16. The summary of octane blending behavior of hydrocarbons and other organic compounds (Ghosh et al., 2006; Boot et al., 2017; Farrell et al., 2019).

	Paraffins	Olefins	Aromatics	Naphthenes	Ethanol	Furans	Cyclic ketones	Esters
Paraffins						2	2	2
Olefins						2	2	2
Aromatics					1	2	2	2
Naphthenes						2	2	2
Ethanol			1					
Furans	2	2	2	2				
Cyclic ketones	2	2	2	2				
Esters	2	2	2	2				

1 Blending would be more linear when the amount of methyl groups increases in the aromatic ring

2 With all hydrocarbons, not specified group

Linear
Synergy
Antagonism
More research

There is not a lot of green colour in Table 16 that indicates that the octane blending of hydrocarbon groups is mainly non-linear. Paraffins blend linearly with paraffins and, also olefins with olefins that can be explained by their similar functionalities. What is interesting in Table 16 is the linear blending of naphthenes with olefins even though their chemical structure, double bonds versus cyclicity, differs from each other significantly. The one possible explanation for that is the possibility of naphthenes to be also olefinic that is seldom separated in the studies. However, the share of those hydrocarbons is low in gasoline, but according to their high RONs and linear blending they could be desired structures in the future.

The non-linear octane blending is still unclear among most of hydrocarbons and, therefore, the research is necessary to obtain the clear trends how hydrocarbons interact with each other in gasoline blends. There have been already found some interactions in Table 16 such as aromatics blend with olefins and paraffins antagonistic, but their blending with ethanol is more complicate, because the methyl groups in aromatic ring could reduce their antagonistic blending and turn it towards linear blending. However,

the universal trend of blending ethanol with aromatics is hard to draw, and more research is needed to measure how large the reduction of antagonism would be. Gasoline can contain only 35 vol% of aromatics and 10 vol% ethanol that demands 55 vol% for other hydrocarbons. They could have an influence on the RON of gasoline that needs to be investigated, because normally aromatics have been noticed to show synergistic blending with ethanol. This synergy could be the solution to compose high RON blends of aromatics and ethanol.

What is also interesting in Table 16 is the blending of aromatic compounds together, because those blends could have higher or lower RON than linear blending indicates. Table 16 shows also that the octane blending of naphthenes together cannot be predicted precisely. Their cyclic structure and different amount of side groups in their structure might be the reasons for that.

In Table 16, oxygenates, ethanol, furans and cyclic ketones, blend non-linearly with hydrocarbons, but mainly synergistically. There is predicted ethanol to blend with paraffins and olefins synergistic and with aromatics antagonistic in Table 16, while its blending with other compounds is still under the research. There is also one oxygenate group, esters, that blends antagonistic with hydrocarbons in Table 16. However, the specific hydrocarbons are not defined that needs more investigation to enable the broad utilization of renewable feedstocks.

As the summary of Table 16 can be concluded that the octane blending of olefins and paraffins with other compounds is the most known. There can be seen in Table 16 that the octane blending of oxygenates needs the most research, but it is understandable, because their use in the gasoline blending is new. In addition to the octane blending, other properties need to consider when gasoline blend are formed. For instance, paraffinic blending components are very light as noticed in the section 6.2, that might be a problem in the blending, because the lower limit for density according to the EN 228 is 720 kg/m^3. Figure 25 shows for instance the density of n- and isopentane to be approximately 640 kg/m^3.

Ethanol has also a significant effect on the DVPE of gasoline blend already with its small concentrations. Ethanol could increase it rapidly with 5 vol% additions, but with the higher volumes DVPE starts to decrease slowly as the thesis has concluded earlier. This turns the ethanol blending even more challenging and limits it with high vapour pressure components like n- and isoparaffins. While aromatics have lower DVPE and their blending with ethanol is more moderate, because aromatics and ethanol form azeotrope mixture. That kind of blending behaviour promotes the aromatics utilization as blending component besides their high RON.

7 Conclusions and proposals for the future study

Gasoline consists of hydrocarbons that can be divided to n-paraffins, isoparaffins, olefins, naphthenes and aromatics. Moreover, ethanol and ethers are added to gasoline to

increase its properties such as RON. High RON is an important property to avoid knocking in the engines, because otherwise it could damage engine parts. Some hydrocarbons have a significant role to mitigate that phenomenon and gasoline blending components that contains these are viable in the gasoline blending.

Highly branched hydrocarbon backbone, the length of the backbone, bonds between carbons, OH-groups and the positions of double bonds and methyl groups in the carbon backbone have been noticed to influence on the reactivity of hydrocarbons. Especially, the thesis noticed the position of methyl groups in aromatics to have an influence on their RON. For instance, RON of ortho-xylene is significantly lower than RON of para- and meta-xylenes, because their methyl groups are not in the adjacent carbons as ortho-xylene has. These compounds with higher RON have low reactivity that reduces their autoignition reactions and the knocking. Therefore, the knowledge of structure of hydrocarbons could help to optimize the RON of gasoline blend. There are also other high RON compounds in gasoline like oxygenates, olefins and isoparaffins. Thus, the main strategies to increase RON of gasoline are to crack long paraffins to shorter ones, add chain branching into hydrocarbon backbone and aromatic ring and to dehydrogenate naphthenes to aromatics.

There are different strategies in the blending of gasoline such as available raw materials, operability of refinery, economy targets and directives. These strategies create the guidelines for the composition and properties of gasoline that blending implements. The FQD requires the RON to be 95 at least and therefore, refineries need to blend gasoline components that have high enough RONs. However, this property is not easy to adjust, because it differs depending on blended gasoline components. They behave together differently in gasoline depending on their hydrocarbon structure that could shift the octane blending from linear to non-linear.

The non-linear blending can be synergistic, the RON of gasoline is higher than linearly assumed, or antagonistic, it is lower. There have been noticed that aromatics blend antagonistic with paraffins and olefins in this thesis but blending of aromatic compounds together is more complicate. While ethanol blends synergistic with paraffins and olefins, but its blending with aromatics is noticed to be antagonistic. Normally, there have been detected synergy between ethanol and aromatics in gasoline blends that could be explained by the methyl groups in aromatic ring. They could reduce the antagonistic blending and turn it more linear or even synergistic. However, deeper understanding of the chemistry behind the non-linear octane blending is necessary to optimize the required RON of gasoline and for that the future research should focus on.

There are guided also the other properties of gasoline such as the density and the DVPE in the FQD and EN 228. The thesis noticed differences between densities of gasoline blending components that need to be considered in the blending to produce gasoline that density is between 720 kg/m^3 and 775 kg/m^3. The DVPE is also an important property, because it defines the volatilization of gasoline components. Higher DVPE increase the volatilization of gasoline and facilitates its ignition. Moreover, the LHV

become more important when the utilization of new renewable feedstocks begins in the future. The LHVs are noticed to be almost same for all fossil gasoline blending components, because they consist of hydrogen and carbon. However, ethanol and ethers have lower LHVs, because they contain also oxygen that reduces the released energy of gasoline during the combustion. The ethanol limit is at maximum 10 vol% according to the FQD that does not cause the significant reduction of the energy release of gasoline. However, its higher addition could increase the consumption of gasoline in the consumer point of view in the future. Therefore, the research of new renewable feedstocks needs to consider the LHVs.

The potential renewable feedstocks into the existing upgrading units are terpenes, ketones and furans. In the hydrotreating units are removed the double bonds from feedstocks and reformation, FCC and isomerization units upgrade the feed into high octane gasoline components. However, some challenges are still present especially in the hydrotreating unit that needs to remove oxygen from furans and ketones. Therefore, the next step could be the development of the catalysts for the HDO in the hydrotreating unit to handle renewable feedstocks and enable the production of more sustainable gasoline in the future.

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